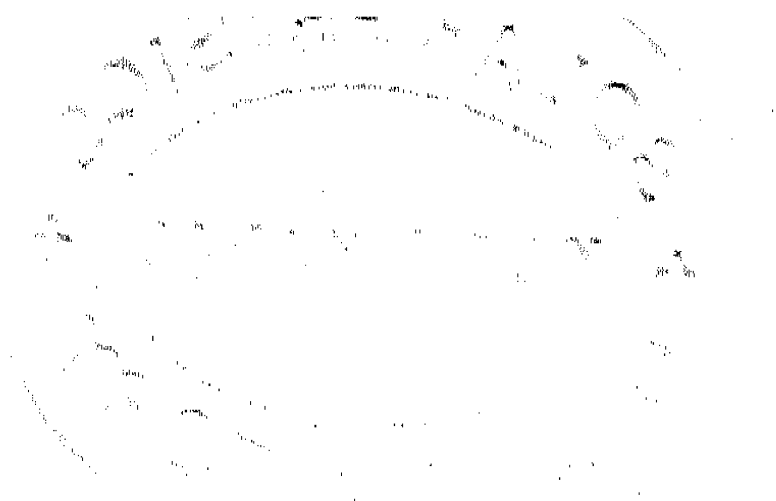


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Professor in the High School for Engineers in Milan

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Volume II

Quantum Theory

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AUTHOR'S PREFACE TO THE FIRST EDITION

THE first two chapters are introductory, and describe those basic ideas in chemistry, physical optics and the electromagnetic theory of light which are needful to a proper understanding of the remaining chapters.

For the sake of simplicity and brevity, some subjects have been omitted altogether, and in others the treatment has been limited to giving the reader a general idea of what is known. If there are gaps, these are not always unintentional ; on the other hand, some repetition has been thought permissible as likely to assist the reader.

In dealing with the principal subjects, each one of which has a separate chapter devoted to it, we have mentioned only the most prominent physicists so as to avoid referring to hundreds of names. At the same time, though the honour of certain theoretical or experimental discoveries may belong chiefly to one man, it is equally true that many others may, by their labours, have prepared the way, may even have reached similar results contemporaneously or have developed and elucidated the work of others.

For such reasons it is sometimes difficult to ascribe names and dates very precisely to the various discoveries ; the progress of science is due to contributions made by many workers, and does not take place solely in vast strides due to single individuals.

Many books on modern physics have already achieved a wide circulation even among non-specialists, particularly those dealing with the advances made during the first three decades of the present century ; in these books just the outstanding points have been dealt with and at no great length.

In the present work the historical and biographical portion,

vi *AUTHOR'S PREFACE TO THE FIRST EDITION*

although of very great interest, has been almost entirely suppressed for the sake of brevity. We have rigidly adhered to the simplest possible form of treatment, avoiding all that is abstruse, all unnecessary elaborations of the argument, and all lengthy calculations which hinder a rapid comprehension of the subject as a whole by obscuring it in a mass of detail.

THE AUTHOR.

MILAN,

December, 1928.

EXTRACTS FROM THE AUTHOR'S PREFACE TO THE THIRD ITALIAN EDITION

IN this third edition I have endeavoured to make the treatment more precise and more vigorous. I have added certain sections, such as those on piezoelectric quartz, photoelectric cells, the new theory of radioactivity, the discovery of parahydrogen, television, etc. . . . The numerical data have been brought up to date. . . . To enable students to follow out the various subjects in greater detail, an extensive bibliography has been added, both in the body of the text and at the end of each chapter; reference is there made to specialist books which are not always available. To assist in the use of the book, the more difficult paragraphs, which do not form an essential part of the main treatment, have been marked with an asterisk and subsidiary matter is printed in smaller type. The less advanced reader may omit Chapters III, VII, VIII, and IX of Vol. II.

THE AUTHOR.

MILAN,

December, 1930.

TRANSLATORS' NOTE

IN consultation with the Author, it has been decided to reduce somewhat the bulk of the work by the omission of Chapters IV, VI and XXI of the third Italian edition. These chapters deal respectively with the Brownian Movement, Relativity and Mass, and Astrophysics. In addition, Chapters III and VIII of Vol. II of the English edition have been slightly abridged. The other alterations and rearrangements made are of a very minor character. The opportunity has been taken to correct certain slight errors in the text and to revise the more fundamental data in accordance with the International Critical Tables.

W. S. STILES.

J. W. T. WALSH.

TEDDINGTON.

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RECENT ADVANCES IN ATOMIC PHYSICS

VOLUME II

CHAPTER I

THERMAL RADIATION AND QUANTUM THEORY

IN Rutherford's model of the atom each electron moves in a closed path around the nucleus ; in the hydrogen atom this path is an ellipse ; according to the classical theory of electromagnetism, then, the electrons should emit radiant energy, and as this emission can only take place at the expense of the kinetic energy of the electrons, their velocity should tend to diminish and they should continually approach the nucleus, describing smaller and smaller paths as time goes on. Such shrinkage of the trajectory should, moreover, cause the velocity of the electrons to increase as a result of the conversion of potential into kinetic energy and hence the frequency of the emitted radiation should increase continuously. This deduction is absolutely contrary to the fact that the radiation emitted from an incandescent gas gives a spectrum of lines, each corresponding to a well-defined wave-length ; on the line of reasoning just described, however, light emitted from a large number of atoms should contain a wide range of wave-lengths and should therefore give a continuous spectrum. There is the further fact that if the electrons closed in on the nucleus during their rotation, the atom would be an unstable system which would suffer spontaneous destruction. This difficulty has been dealt with by the Danish physicist N. Bohr in a way which we shall describe in a later chapter.

We are faced with no less a dilemma than the following : either we must admit that the laws of the classical electrodynamics, which have been verified without exception in every branch of physics, do not apply to the motion of an electron, or else we must

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abandon Rutherford's model of the atom, which has given such a satisfactory explanation of all the known facts. This was the problem that presented itself in 1913 ; but the difficulty of having to assume that the laws of classical mechanics (*i.e.*, those propounded by Galileo, Newton and Maxwell) could not be applied in their simple form to atoms and electrons considered individually had been faced, towards the end of 1899, by another great physicist, viz., Max Planck of Berlin. He, in order to account for the spectrum given by a black body,* had already been forced to introduce a completely new, almost revolutionary, idea into physics, and this had become so well established that when Bohr proposed his theory, contradicting the fundamental ideas which had so completely dominated the nineteenth century, physicists were not surprised, the more so as Bohr's postulates were in perfect accord with Planck's theory. Classical physics, that wonderful structure which had survived the attacks of centuries, was found to be inadequate when applied to the atomic universe. A few years later that same physics, founded by Galileo and Newton, was to be found untenable in the study of velocities comparable with the velocity of light.

In view of these facts, the reader will understand why we have considered it desirable to interrupt our logical development of the theory of the atom in order to explain in full Planck's theory which gave birth to the " quantum " theory, the pivot of modern physics ; Planck's work is revolutionary, marking, as it does, the supplanting of the old physics by the new.

The famous physicist, when he published his work on black body radiation in 1900, certainly had no idea of the vast consequences which would follow ; actually the quantum theory had its origin in Planck's successful attempt to explain the experimental results concerning the distribution of energy in the spectrum of the *black body*.

We shall, then, postpone to the following chapters our development of Bohr's theory and of its subsequent improvements,

* The name " black body " is applied to a body which can absorb all the radiation incident on it ; lamp black very nearly complies with this definition,

in order to give a concise account of Planck's theory and its consequences.

The Birth of the Quantum Theory. Planck's Work on the Black Body

In order to facilitate the perusal of this chapter, it will be desirable to give a brief synopsis of the contents, so that the reader may follow the logical connection between the various paragraphs without losing sight of it in the maze of details.

A small hole is made in a hollow body raised to a uniform high temperature ; the interior is seen to be incandescent and it is well known that all bodies contained in such a furnace appear to be of the same colour.

This colour, this radiation due to incandescence, are characteristic of the temperature of the furnace and are independent of the nature of the substance heated. If this radiant energy be analysed, it will be found to be complex, containing a vast range of monochromatic radiations, visible and invisible, each present in definite intensity so that the total radiation has a definite spectral distribution. It is possible to measure the intensity of each radiation and then to draw a curve representing the distribution of energy among the various wave-lengths present, and this had been done in 1899 by Lummer and Pringsheim. The curve so found was bell-shaped, having a pronounced maximum at a wave-length intermediate between the upper and lower limits.

When the temperature is raised, the total energy varies as the fourth power of the temperature and, at the same time, the radiation corresponding to the peak of the curve moves towards the shorter wave-lengths ; this latter fact expresses the experimental result that as the temperature of an incandescent body is raised it at first becomes deep red, then orange-red, then pale red and finally white.

Theoretical physicists vainly attempted, from 1900 onwards, to give a mathematical explanation of this result ; to give such an explanation meant discovering the law according to which the energy comprised within a certain wave-length interval, varied

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with the wave-length itself, and with the temperature of the enclosure. In order to obtain this special distribution law the light waves must be thought of as electromagnetic and as originating in the vibrations of electric oscillators situated in the walls of the isothermal enclosure under consideration ; similarly, by the principle of resonance, an electric oscillator can absorb light waves which have the natural frequency of the oscillator.

If this idea be expressed mathematically and if it be remembered that, in a state of equilibrium, the oscillators obviously must receive from the ether just as much energy as they emit, then by applying the electromagnetic theory an energy distribution is obtained which is in complete disagreement with that found experimentally.

In order to explain the experimental results, which had been thoroughly established by 1900, Planck was forced to introduce a new and extraordinary theory, viz., that the resonators supposed to be situated in the incandescent material, instead of having *any* amount of energy, W , as was supposed in the classical electrodynamics, *could only have discrete amounts of energy, i.e., amounts differing by steps or by equal jumps*, each step being equal to the product of a constant h multiplied by the frequency of the oscillator. Further, if each step had the value $h\nu$, an oscillator could only have an amount of energy which was a multiple of $h\nu$, i.e., $nh\nu$.

This constant h , introduced by Planck in 1900, has a definite value ; it is called Planck's constant (6.55×10^{-27} erg \times sec.), and is now of supreme importance in all modern physics. We shall see, as this book proceeds, the vast consequences of Planck's idea.

We may at once clear the ground of a slight difficulty ; h is also called the "quantum of action" for the following reason : in mechanics *action* is the name given to the integrated sum of the successive values assumed by the product *momentum* $\times \Delta t$ in just the same way as work is the integral of $f \times ds$.

Now considering the equation $W = nh\nu$ it will be seen that h is the quotient of energy by frequency : since the latter quantity is the reciprocal of time, it follows that the dimensions of h are

energy \times time, *i.e.*, action. Strictly speaking, then, Planck postulated a discontinuous variation, a variation *per saltum*, not for energy but *for action*.

It is for this reason that the expression " $\text{erg} \times \text{sec.}$ " was written after the value $h = 6.55 \times 10^{-27}$, just as $\text{cm.} \times \text{sec.}^{-1}$ is written after a velocity expressed in C.G.S. units.

Now that we have given a brief account of the origin of Planck's theory we shall pass on to deal with its development and its final conclusion.

Résumé of the Elementary Theoretical Considerations Regarding Radiation

When radiation falls on the surface of a body, a sudden change of direction takes place and there may be reflection, refraction and, if the radiation is sent back in all directions, diffusion.

The properties of monochromatic radiation are especially simple when it is polarised; in this case light is represented by a vector, called the light vector, which is perpendicular to the ray, and of which the length varies with the time according to the well-known sine relationship; the energy carried by the radiation in one second is proportional to the square of the amplitude of this vector; the light vectors corresponding to a single ray are additive according to the rule for the addition of vectors.

For this reason every non-polarised light ray may be considered as composed of two rays polarised at right angles to each other, with planes of polarisation which vary continually in any second, but are always mutually perpendicular; the intensity is double that of each of the two individual rays.

Looked at from another point of view, in the electromagnetic theory it is shown that a light ray is simply an electromagnetic wave which carries with it the two vectors, electric force and magnetic force, perpendicular to each other and in the plane normal to the ray.

Let us now turn to the interesting phenomenon called the *pressure of radiation*. When a beam of radiation, composed of a bundle of parallel rays, falls on the surface of a body the electromagnetic field present in the radiation exerts forces on the electrons contained within the body and the resultant of these forces is equivalent to a pressure, the *pressure of radiation*.

Starting from Maxwell's well-known equations, it can be shown mathematically that, for a perfectly reflecting surface, this pressure is always normal to the plane of the surface whatever be the angle of incidence i (the angle between the radiation and the normal to the surface). The magnitude of the pressure is $p = u \cos^2 i$, where u is the energy density, *i.e.*, the quantity of energy per cubic cm. in the neighbourhood of the surface. This density is made up of both the incident and the reflected radiation, these two being equal to each other. In the case of a perfectly reflecting body placed outside the earth's atmosphere and exposed perpendicularly to the solar radiation, the above formula becomes $p = u$. Now it is known that the energy received per square cm. under these conditions is 1.35×10^6 ergs per sec., and since this quantity of energy is contained in a cylinder of length equal to the velocity of light (3×10^{10} cm.) the density of the incident energy is $(1.35 \times 10^6)/(3 \times 10^{10}) = 4.5 \times 10^{-5}$ erg per cubic cm.

In order to find u the above value must be doubled, since the reflected energy

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is equal to that received ; it is thus found that $u = 10^{-4}$ dyne per sq. cm. ; the pressure on a square metre would be 10,000 times as great, *i.e.*, about one dyne (one thousandth of a gram).

In spite of the smallness of these pressures, they have been shown to exist by means of the well-known experiments of Lebedew, Poynting, Nichols, Hull and others.

Emissive Power, Absorbing Power, Incandescence, Luminescence

Let ds be a small element of the surface of a body, dS the area projected on a plane perpendicular to the normal to the surface and $d\omega$ an infinitely small solid angle containing this normal. The energy emitted per second from this area, within the solid angle, is clearly proportional to dS and $d\omega$ for any given monochromatic polarised radiation ; it is also proportional to the interval $d\lambda$ between the limits λ and $(\lambda + d\lambda)$ which define the monochromatic radiation ; thus the energy is expressed by $dw = e_\lambda \cdot d\lambda \cdot dS \cdot d\omega$ ergs per sec. The coefficient e_λ is called the emissive power. Suppose now that the element ds receives radiation which is identical with that just considered, comprised within the same wave-length interval $d\lambda$, travelling in precisely the opposite direction and polarised in the same plane, then part of the incident energy will be reflected diffusely, part will be returned on its path and, finally, part will be *absorbed* ; the ratio a_λ of the energy absorbed to the incident energy is the *absorbing power* of the body for the particular direction, wave-length and plane of polarisation considered.

It is found experimentally that this absorbing power is independent of the quantity of energy falling per second on the element of surface ; it is this fact that gives meaning to the definition.

When a body radiates by purely thermal incandescence, all the energy radiated by it comes from the heat it contains ; the only energy changes which such a body can undergo are gain or loss of heat ; thus the emissive power and the absorbing power corresponding to any given point of the surface, to a given direction and a given wave-length are functions of the temperature alone. Hence if the temperature be kept constant, the body will radiate for ever in the same manner.

If, however, the source of the radiated energy be chemical, electrical or luminous, the phenomenon is one of luminescence ; such, for example, are the oxidation of phosphorus, the light of the electric arc, fluorescence, etc.

In the case of purely thermal radiation we shall see presently that by simply applying the principles of thermodynamics we can construct a complete picture of the laws governing heat emission.

In a Closed Isothermal Enclosure the Radiation is in Statistical Equilibrium

In a solid, closed and opaque enclosure, maintained at constant temperature (*i.e.*, rendered isothermal)—as, for instance, by surrounding it with boiling water—the *internal* temperature has a definite meaning whether the enclosure contains matter or whether it be entirely evacuated ; a thermometer gives the same reading when placed in the middle of the enclosure as it does when placed against the walls. The same is true whether the enclosure

be of copper or of porcelain, large or small, spherical or polyhedral or of any other form.

Whatever may be the initial distribution of temperature in the system, it finally attains a state of equilibrium or, rather, a *stationary* state in which radiation passes through each square centimetre of the inner surface in such a way that the energy which crosses it from right to left is equal to that which crosses it in the opposite direction.

Consider an element of surface dS at any point on the inside of an isothermal enclosure and let an elementary cone of angular aperture $d\omega$ be constructed so as to enclose the normal to this element dS . The quantity of energy which passes through dS per second and which is contained within the solid angle $d\omega$ is completely defined, for radiation defined by the wave-length limits λ and $(\lambda + d\lambda)$ as follows :

$$dw = E_{\lambda} d\lambda dS d\omega,$$

where E_{λ} is independent of the position of the point, of the orientation of the elementary area and of the material of the enclosure. It can be shown, however, that this function E_{λ} depends on the nature of the medium which fills the enclosure (*e.g.*, air, water or carbonbisulphide).

We will now suppose that the enclosure is entirely evacuated so that the specific intensity E_{λ} is a function of two variables only : the absolute temperature of the enclosure, T , and the wave-length ; this is expressed symbolically as follows :

$$E_{\lambda} = F(\lambda, T)$$

This can be expressed quite simply by saying that, at a given temperature, the different wave-lengths convey different quantities of energy through unit area and within unit solid angle ; the same wave-length interval conveys different amounts of energy at different temperatures.

The function F is that function which expresses the law of energy distribution.

Kirchhoff (1824–1887) was well aware of the great importance of being able to determine this function $E_{\lambda} = F(\lambda, T)$, for it is the expression of a *universal law* relating to exchanges between matter

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and ether, one which is quite independent of any particular property of the material of the enclosure. "Es ist eine Aufgabe von höher Wichtigkeit diese Funktion zu finden," he wrote,* but forty years were needed to solve the problem.

The series of attempts to determine the energy distribution in the black body spectrum came to an end when Planck, in 1900, as we shall see, succeeded in obtaining the function $F(\lambda, T)$ mathematically after it had been found empirically by means of a large number of laborious experimental investigations.

It can be shown that E_λ for a vacuum can be obtained from the value of E'_λ for any given medium by means of the equation :

$$E'_\lambda/n_0^2 = E_\lambda$$

where n_0 is the index of refraction of the medium at the wave-length λ with respect to a vacuum.

Total Energy of Radiation in a Closed Space and the Energy Density

The total energy w for the whole radiation may be obtained by summing the energies appropriate to all the wave-length intervals $d\lambda$; this sum is

$$W = 2Sd\omega \int_0^\infty E_\lambda d\lambda,$$

The coefficient 2 is inserted because E_λ refers—as has been said—to polarised light; the energy of natural unpolarised radiation is, as we know, double this.

In order to obtain the *density of the energy*, i.e., the quantity of energy contained in a cubic centimetre, it must be remembered that all the elements of energy dw which go to make up the total w are composed of narrow cylindrical bundles of rays the height of which is equal to c , the velocity of light in a vacuum.

For an area of one square cm. and a height of one centimetre, then, the energy is :

energy density for unit

solid angle $d\omega$

$$du = 2(E_\lambda/c)d\lambda d\omega$$

and, taking into account all possible directions in space, the solid

* "It is a problem of great importance to find this function."

angle becomes 4π , so that, dealing throughout with only the wave-length interval $d\lambda$,

$$\begin{aligned} u &= 2(E_\lambda/c) d\lambda \int_0^{4\pi} d\omega \\ &= 2(E_\lambda/c) d\lambda \cdot 4\pi, \end{aligned}$$

and thus, finally, the total energy density for all wave-lengths becomes :

$$\text{Total energy density} \quad U = (8\pi/c) \int_0^\infty E_\lambda d\lambda.$$

Kirchhoff's Law (1850) and the Black Body

We shall here confine ourselves to giving, without proof, Kirchhoff's famous law which states that the ratio of the emissive power to the absorbing power (e_λ/a_λ) is the same for all bodies surrounded by the same medium, provided both quantities are measured at the same point of the body and refer to the same wave-length and the same plane of polarisation; actually this ratio is equal to the specific intensity of the radiation considered, E_λ , in the medium surrounding the body.

Thus $e_\lambda = a_\lambda E_\lambda$. This important relationship is almost self-evident, since, if we consider a body immersed in an isotropic and homogeneous medium, then for every direction, for every plane of polarisation, and for every wave-length, the quantity of energy emitted must be equal to that present in the medium multiplied by the absorption coefficient; for, clearly, in a steady state the energy absorbed by the body must be restored to the medium.

It follows at once that, for a body which can wholly absorb a monochromatic radiation, a is unity, and hence the emissive power is equal to the specific intensity E_λ of the medium.

The black body is a body which absorbs the whole of any radiation; hence, since the specific intensity E is independent of the plane of polarisation, the emissive power is equal for all planes, *i.e.*, the energy emitted is unpolarised. Further, E_λ is independent of direction, and consequently the emissive power of the black body is the same in all directions.

It is better to use, instead of the name black body, the term

“total radiator,” since at a sufficiently high temperature the black body emits visible light, and this is inconsistent with the more familiar name.

It will now be understood how important the conception of the black body may become in practice ; since $e_\lambda = E_\lambda$ the normal radiation from the space inside an enclosure such as we have described above, *i.e.*, the function $E_\lambda = F(\lambda, T)$ is identically the same as the radiation from a black body into space ; the function $F(\lambda, T)$ therefore represents also the distribution of energy in the black body spectrum.

This result is of the greatest practical importance. It is known that there is no body which absorbs completely at every wave-length ; a surface covered with a thick layer of lamp black is very nearly a black body for visible radiation and for that near the visible spectrum ; even lamp black, however, has an appreciable reflecting power for radiation at long wave-lengths. In order to obtain a perfectly black body, however, it is sufficient to take a hollow enclosure of some opaque material, to maintain this at a constant temperature and to make a very small hole in the walls to serve as a window ; the distribution of radiation inside the enclosure is then the same as if it were completely closed and the radiation from the hole is identical with that which would be emitted from a black body at the same temperature. On the other hand, none of the radiation which enters the body from outside through the hole can escape, since it undergoes an infinite series of reflections within the enclosure and consequently is completely absorbed ; the hole acts as a black body and is a perfect absorber. A hollow steel sphere, heated externally by immersing it in steam or by means of an electric current, and having a small hole at some point in the wall, is a practical form of total radiator.

Stefan's Law *

In giving an explanation of the two fundamental laws due to Stefan and to Wien, we shall state everything that can be found

* Discovered empirically by Stefan (1835-93) and demonstrated mathematically by Boltzmann (1844-1906).

out regarding the energy distribution in the black body spectrum, *i.e.*, regarding the function $E_\lambda = F(\lambda, T)$, as a result of applying purely thermodynamical considerations. We shall show, too, that the form of this function cannot be settled by the application of the principles of thermodynamics alone; it is the quantum theory, proposed by Planck, that enables E_λ to be completely determined, and it was Planck who, in fact, succeeded in determining it.

Consider an empty enclosure (Fig. 1) made of any material and having a cylinder with a piston which is considered to be a perfect reflector; the enclosure is filled with isothermal radiation.

If the piston be moved, T changes; we shall see presently that the quantity of energy radiated into the enclosure within unit solid angle per second and per unit area is given quite simply by the expression σT^4 where σ is a constant; this energy, then, varies as the fourth power of the absolute temperature.

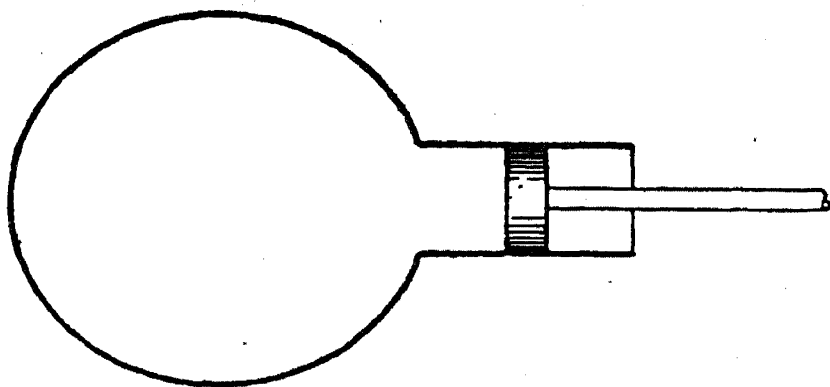


FIG. 1.

The total energy radiated by a black body can thus be found, and hence Stefan's well-known law is obtained.

In order to prove what has been stated above, we will first calculate the pressure of radiation on the piston when stationary; this is

$$dp = (U/2\pi) \cos^2 i \cdot d\omega \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for a small solid angle $d\omega$ enclosing the direction of incidence, the latter being at an angle i with the normal. As we know, U is the total energy density and is given by (see p. 9),

$$U = (8\pi/c) \int_0^\infty E_\lambda d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In order to obtain the total pressure per square cm., all possible directions of incidence must be taken, *i.e.*, the differential

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equation (1) must be integrated *; we thus obtain quite easily :

$$\text{Total pressure of radiation } p = \frac{1}{3}U \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

What we wish to find, however, is the relation between the energy density and the temperature; for this purpose, consider a displacement of the piston such as to cause a variation of volume dV ; the quantity of heat dQ supplied to the system is the sum of the work done, $p dV$, and the change produced in the radiant energy contained in the system, viz., $dW = d(U \cdot V)$. Thus :

$$dQ = dW + p dV = (U dV + V dU) + p dV.†$$

Hence, making use of equation (3), the change in the entropy (dQ/T) is found to be given by :

$$\frac{dQ}{T} = \left(\frac{V}{T} \frac{dU}{dT} \right) dT + \frac{4}{3} \frac{U}{T} dV$$

Now the entropy of a body is a function which always takes up the same value when the body returns to the same state; it is therefore an exact differential and depends on the two variables (temperature and volume) in such a manner that its expression, as written above, has the classical form of exact total differentials. It follows that :

$$\frac{\partial}{\partial V} \left(\frac{V}{T} \cdot \frac{dU}{dT} \right) = \frac{\partial}{\partial T} \left(\frac{4}{3} \frac{U}{T} \right) = -\frac{4}{3} \frac{U}{T^2} + \frac{4}{3} \frac{dU}{dT} \cdot \frac{1}{T}$$

From the last equation we obtain at once

$$\frac{dU}{dT} = 4 \frac{U}{T} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

This gives, on integration, $U = aT^4$ where a is a constant. If now we consider the surface of a black body, the energy it radiates per second over an element of area dS , taken normal to the elementary cone of angular aperture $d\omega$, is given by

$$2dS d\omega \int_0^\infty E_\lambda d\lambda = 2dS \cdot d\omega (cU/8\pi)$$

* By considering two coaxial cones having semi-vertical angles i and $(i + di)$, and their axes coincident with the normal to the surface, it will be seen that $d\omega = 2\pi \sin i \cdot di$.

† For $W = U \times V$ so that $dW = U dV + V dU$.

(see p. 9), and since the energy density U varies as the fourth power of the temperature, a simple integration enables us to express W , the total quantity of energy radiated per second in all directions by a black body, i.e., it gives us Stefan's law.

$$\text{Stefan's law} \qquad W = \sigma T^4$$

where σ is Stefan's constant.

This well-known law has been verified over a wide range of temperatures, about 2,000 degrees; the verification consists in receiving, in a *total absorber*, the energy radiated by a black body. The absorber may consist of a cone (of vertical angle 30°) with the walls blackened so that the radiation received is completely absorbed by them owing to the repeated reflection; the radiation is directed along the axis of the cone. It is found that, for a definite solid angle $d\omega$ and a certain area dS receiving radiation (the desired value of dS is obtained by an appropriate system of screens), the energy received by the absorber varies as the fourth power of the absolute temperature.

Actually, if the absorber is maintained at the temperature T , the quantity that is measured is $W = \sigma(T^4 - T_1^4)dS \cdot d\omega$, i.e., the difference between the energy received and that re-emitted, for the absorber also acts as a radiator; however, if T_1 is very small compared with T , its fourth power may be neglected with respect to T^4 * and the experiment is somewhat simplified.

A large number of experiments have given the value 5.72×10^{-5} for the constant σ .

From measurements of the solar energy received at the earth's surface it is found that the sun emits 6.25×10^{10} ergs per second per square cm. of surface; further, from the curve of energy distribution it is known that the sun radiates approximately as a black body. Its temperature may therefore be calculated from the equation $W = \sigma T^4$.

Putting $W = 6.25 \times 10^{10}$ and $\sigma = 5.72 \times 10^{-5}$ we find $T = 5750$ degrees absolute.

Let us return for a moment to the pressure of radiation; this is

* E.g., if $T_1 = 288$ i.e., 15° C.) and $T = 910$ (i.e., 637° C.).

It follows from equation (1), that, if we consider a small range of wave-lengths $d\lambda$, since every wave-length changes in the same ratio, the same proportional change applies also to the range $d\lambda$, hence this range is altered by a proportionate amount which is the same at all wave-lengths and which is given by

$$\frac{\Delta(d\lambda)}{d\lambda} = \frac{\Delta\lambda}{\lambda} = \frac{1}{3} \frac{\Delta V}{V} \dots \dots \dots (2)$$

In other words, if the volume is increased by one-thousandth of its original value, every wave-length is increased by $\frac{1}{3000}$ and, equally, a small monochromatic interval is lengthened by $\frac{1}{3000}$ of its original value.

It is therefore easy to find how a change of volume, and hence also a change of temperature, changes the relation connecting the specific intensity E_λ with the wave-length λ .

Let us suppose that the volume of the enclosure undergoes an adiabatic change, *i.e.*, one which involves no transfer of heat in either direction. The work done on the piston by the pressure of the radiation is $p \cdot \Delta V = \frac{1}{3}U \cdot \Delta V$ since the pressure p is equal to $\frac{1}{3}U$ (see p. 12).

Since this work is equal to the loss of internal energy, *viz.*, $u \cdot V$, we have the relation

$$\frac{1}{3} u \Delta V = - \Delta(uV) = - \Delta u \cdot V - \Delta V \cdot u$$

$$\text{i.e.,} \quad \frac{4}{3} \frac{\Delta V}{V} + \frac{\Delta u}{u} = 0$$

and, hence, referring to (2),

$$4 \frac{\Delta(d\lambda)}{d\lambda} + \frac{\Delta u}{u} = 0 \dots \dots \dots (3)$$

But the density of a monochromatic radiation is connected with the specific intensity E_λ by the relation $u = (8\pi/c)E_\lambda d\lambda$, and this gives :

$$\frac{\Delta u}{u} = \frac{\Delta(d\lambda)}{d\lambda} + \frac{\Delta E_\lambda}{E_\lambda},$$

so that, combining this with equation (3),

$$5 \frac{\Delta\lambda}{\lambda} + \frac{\Delta E_\lambda}{E_\lambda} = 0.$$

On integrating, this equation gives at once :

$$E_{\lambda} \cdot \lambda^5 = \text{const.} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

As stated above, when the piston is displaced, every wave-length is multiplied by the same factor K ; but equation (4) shows that the corresponding value of E_{λ} must be multiplied by K^{-5} in order that the product $E_{\lambda} \cdot \lambda^5$ may be unchanged ; taking these two facts together it follows that *the normal spectral distribution curve*

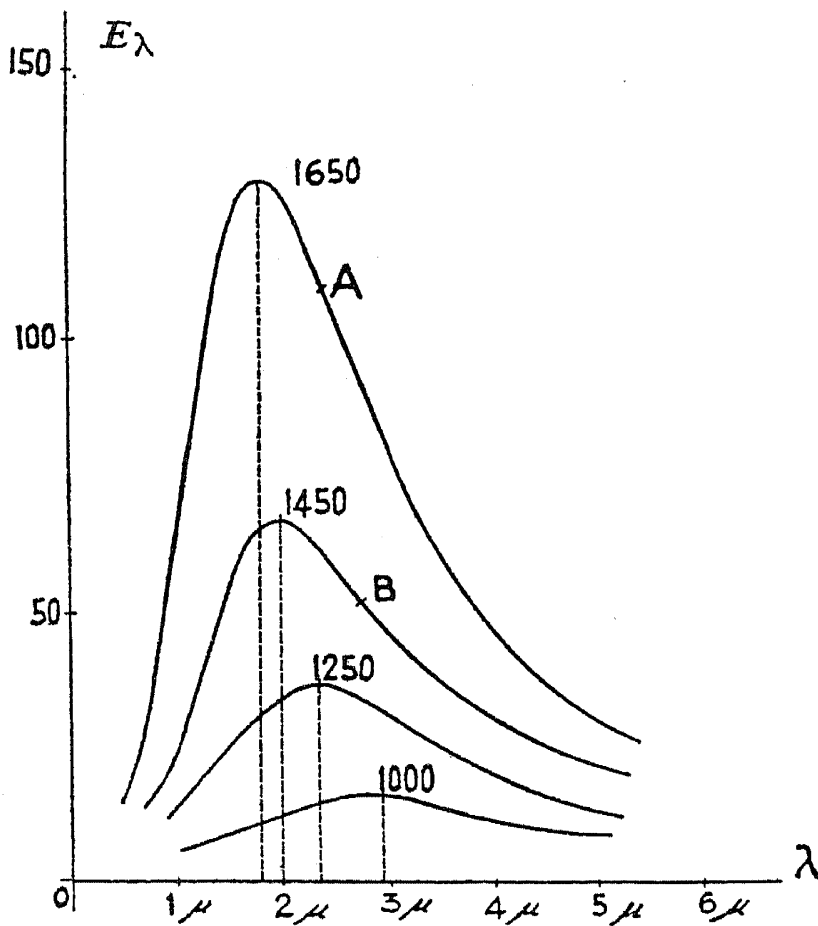


FIG. 2.

corresponding to one temperature T_1 may be changed to the curve for another temperature T_2 by multiplying all the abscissæ (λ) by a constant K , and the ordinates (E_{λ}) by K^{-5} . The total area enclosed by the curve is multiplied by K^{-4} . Further, Stefan's law shows that this constant K is equal to (T_1/T_2) for, when the temperature is altered, the total quantity of energy radiated by a black body, changes in the ratio (T_2^4/T_1^4) and the spectral distribution of the black body is the same as that of the enclosure we are considering.

To sum up : the curve showing the energy distribution (E) at the temperature T_1 gives the curve appropriate to the temperature T_2 if the abscissæ (λ) be multiplied by (T_1/T_2) and the ordinates (E) by $(T_1/T_2)^{-5}$.

Thus a point A on the curve for $1,650^{\circ}$, for instance, gives the corresponding point B on the curve for $1,450^{\circ}$ by using the method of conversion above described (see Fig. 2).

For every pair of corresponding points, λT is constant and so

is E_λ/T^5 by virtue of equation (4); *all the maxima of the curves shown in the figure are corresponding points.*

For all the maximum points, M, we have

$$\lambda_m T = b \quad E_m = BT^5 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where b and B are constants.

These equations have been verified experimentally with great precision; the value of b is 2,885 if λ be expressed in microns.

On passing from one curve to another, as the temperature of the black body rises, the wave-length of maximum intensity in the emitted radiation becomes shorter; thus, as is well known, the black body, as it is heated more and more, emits radiation in which the red at first predominates and then gradually the higher frequency parts of the spectrum appear and, in their turn, become predominant.

Wien's law is often written in the following form :

$$\lambda_m T = 0.2885,$$

where λ is now expressed in cm.

From Wien's law it can be deduced that for all points for which E_λ/T^5 has the same value, λT is constant; *i.e.*, if E_λ/T^5 is known, λT is given. This may be expressed analytically by saying that E_λ/T^5 is a single function of the product λT :

$$E_\lambda/T^5 = \alpha f(\lambda T)$$

$$\text{or} \quad E_\lambda = \alpha T^5 f(\lambda T) \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where α is a constant.

Hence if, from every isothermal, a curve be constructed with values of λT as abscissæ and the corresponding values of E_λ/T^5 as ordinates, *the same curve is obtained in each case.*

This has been verified experimentally.

If we put $f(\lambda T) \cdot \lambda^5 T^5 = \phi(\lambda T)$, equation (6) takes the following form :

$$E_\lambda = \alpha \lambda^{-5} \phi(\lambda T) \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This equation (7) summarises all the information that can be obtained from thermodynamical considerations as regards the

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form of the function E_λ ; further progress can be made only by assuming some hypothesis as to the mechanism of the emission and absorption of radiant energy.

It is this hypothesis that we shall deal with in the next section; it is the essential part of Planck's theory and the outstanding work of that celebrated physicist.

We have already seen that the temperature of the sun may be deduced by applying Stefan's law; it can be also found by applying the displacement law, again regarding the sun as a perfect radiator. Measurements of solar radiation carried out with the spectrophotometer show that the wave-length of maximum radiation is 4.70×10^{-5} cm.; from the equation $\lambda_m = 0.2885/T$ we find that $T = 6150$ degrees absolute.

Energy Distribution in the Black Body Spectrum. Planck's Theoretical Investigations the Starting Point of the Quantum Theory

Before Planck succeeded in solving the problem of finding the true form of the function of λ and T which gives E_λ , a number of formulæ had already been proposed by different scientists during the last decade of the century just passed; we may mention the names of Wien, Lord Rayleigh, Jeans, etc. These formulæ, however, were based on the classical method of mechanics and not on the quantum mechanics.

The experimental test of these formulæ for $E_\lambda = f(\lambda T)$ was applied by constructing the so-called isothermal curves (similar to the bell-shaped curves already shown) which give the specific intensity E_λ for every wave-length when the temperature is constant. The experimental curve for one given temperature being known the other curves were obtained by applying Wien's law.

By this method *isochromatic curves* were then constructed for checking the proposed formulæ; these curves give, for any temperature, the intensity of the radiation at a certain wave-length (*e.g.*, $\lambda = 26$ microns, a monochromatic radiation which passes through fluorite); these experiments were carried out over a vast range of temperatures, from the boiling point of liquid air to 1,500 degrees.

We will not, for the moment, quote the formulæ due to Jeans

$$E_{\lambda} = \frac{hc^2 \lambda^{-5}}{e^{\frac{N}{R} \frac{hc}{\lambda T}} - 1} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1)$$

h = a universal constant.

When the stationary state has been reached in the enclosure, this radiation results from the equilibrium established between the radiation emitted from the walls and the radiation absorbed. Planck, in order to obtain an expression for the equality between the energy radiated and that absorbed by the walls, assumed that the property of emission and absorption possessed by the walls was due to the existence of an infinite number of small rectilinear electric oscillators each having its own natural period; each oscillator consists of an electric charge the movement of which is accompanied by the *emission* of an electromagnetic wave, *i.e.*, light; conversely, the oscillator behaves as a resonator and is set in vibration by an external field from which it *absorbs* light of a frequency equal to its own natural frequency. Making these assumptions, Planck, in 1900, succeeded in showing that, if we consider those resonators which give rise to the various wave-lengths lying within the range λ to $(\lambda + d\lambda)$, and if we take

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the mean value w of their energy in the steady state, the following relation holds in the case of a vacuous enclosure :

$$E_{\lambda} = c.w./\lambda^4 (2)$$

where c is the velocity of light *in vacuo*.

It is to be remembered that E_{λ} represents, as usual, the specific intensity for polarised light. Now the oscillators, which are in equilibrium with the energy contained in the enclosure, would also be in equilibrium with a gas if this occupied the enclosure, and we know that the average kinetic energy of gas molecules is $\frac{3}{2}(R/N)T$.

The whole system of oscillators has an infinite number of degrees of freedom, since each oscillator has one ; under these conditions, by the principle of the equipartition of energy, the same quantity of energy, on the average, is present in each of the degrees of freedom and this energy is half potential and half kinetic, as in the case of a swinging pendulum.

The total energy of an oscillator, irrespective of the frequency, is therefore RT/N ,* just as if this energy were maintained by the direct impacts of the gas molecules which might be supposed to fill the enclosure.

Equation (2) therefore becomes $E_{\lambda} = (R/N) c (T/\lambda^4)$, which is an impossibility because, if it were true, as the wave-length diminished the intensity emitted would increase to infinity, whereas it is well known that the intensity of the radiation in the black-body spectrum is small at the low frequencies corresponding to red light and is also small for the violet radiations of high frequency. In other words, E ought to tend to zero as a limit with diminishing λ .

The formula just given above, deduced by taking the principle of the equipartition of energy as a basis, was thus not in accordance with the facts and had to be rejected. Science was confronted with a difficult problem, and Planck attacked it ; it was the first time that the apparently inexhaustible and self-consistent

* Since there is *one* degree of freedom for each oscillator, we take one-third of $\frac{3}{2}(R/N)T$ and double the result.

system of hypotheses, which formed the basis of mechanics and electrodynamics, had led to an impossible result; Planck realised that there was some flaw in the reasoning; the principle of equipartition could not be applied to the atomic bonds between matter and energy.

He then introduced a new hypothesis and assumed that the emission and absorption of energy by an oscillator (such as he had supposed) took place in such a way that the oscillator could only give out or take up quantities of energy which were exact multiples of the quantity $h\nu$, where h was a universal constant and ν the frequency of the radiation—and therefore the natural frequency of the oscillator as well. The energy of the oscillator, then, could no longer vary continuously but only by steps, or by *quanta*, and it could only be $h\nu$, $2h\nu$, $3h\nu$, and so on.

This means that there is not equipartition of energy among the oscillators having the same frequency; some have energy $\epsilon = h\nu$, others $2h\nu$, and so on. Out of a total number n of oscillators of frequency ν , the laws of probability enable us to calculate how many possess energy ϵ , how many possess energy 2ϵ , and so on.

Actually the probability that an oscillator will have an amount of energy w is proportional to $e^{-(N/RT)w}$, so that the numbers of oscillators, n_1 , n_2 , n_3 , . . . which have respectively one, two, three . . . *quanta* of energy, are given by

$$\left. \begin{aligned} n_1 &= n_0 e^{-(N/RT)\epsilon} \\ n_2 &= n_0 e^{-(N/RT)2\epsilon} \\ n_3 &= n_0 e^{-(N/RT)3\epsilon} \end{aligned} \right\} \dots \dots \dots (3)$$

where n_0 is a constant defined by the fact that the total number n of oscillators is equal to

$$n_1 + n_2 + n_3 + \dots$$

Hence

$$n = \frac{n_0}{1 - e^{-(N/RT)\epsilon}} \dots \dots \dots (4)$$

The total energy W of the n oscillators is given by the sum of the energies and is therefore found from :

$$\text{Total energy } W = n_1\epsilon + n_2 \cdot 2\epsilon + n_3 \cdot 3\epsilon + \dots$$

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By means of very simple transformations, which are given in full in the footnote,* it is found that

$$W = \frac{n\epsilon}{e^{(N\epsilon/RT)} - 1} \quad \dots \quad (5)$$

making use of equations (3) and (4).

It follows that the *average* energy of all the resonators is

$$\begin{aligned} \text{average energy of an oscillator } w &= \frac{W}{n} = \frac{\epsilon}{e^{(N\epsilon/RT)} - 1} \\ &= \lambda^{-1} \frac{hc}{e^{(N/R)(hc/\lambda T)} - 1} \end{aligned}$$

since $\epsilon = h\nu = hc/\lambda$.

Finally, on substituting this value for w in equation (2), which—it is to be noted—still holds and does not depend on the equipartition of energy, we obtain

$$\text{Planck's formula } E_\lambda = hc^2\lambda^{-5} \frac{1}{e^{(N/R)(ch/\lambda T)} - 1} \quad \dots \quad (6)$$

This is Planck's well-known formula, in which N is Avogadro's number, c is the velocity of light in a vacuum, R is the universal gas constant and $h = 6.55 \times 10^{-27}$ erg. sec.

When λT is small, Planck's formula reduces to

$$E_\lambda = A\lambda^{-5} e^{-B/\lambda T}$$

and this is Wien's expression. It agrees with the experimental results in the ultra-violet part of the spectrum at ordinary values of the temperature T . When, on the other hand, λT is large,

* The total energy of the n oscillators is $W = n_0 \times 0 + n_1\epsilon + n_2 \cdot 2\epsilon + n_3 \cdot 3\epsilon + \dots$ or, since $n_1 = n_0 e^{-(N/RT)\epsilon}$, etc.,

$$W = n_0\epsilon e^{-(N/RT)\epsilon} [1 + 2e^{-(N/RT)\epsilon} + 3e^{-(2N/RT)\epsilon} + \dots].$$

But

$$1 + 2e^{-(N/RT)\epsilon} + 3e^{-(2N/RT)\epsilon} + \dots$$

$$= \frac{1}{\{1 - e^{-(N/RT)\epsilon}\}^2}$$

and hence

$$W = \frac{n_0\epsilon e^{-(N/RT)\epsilon}}{\{1 - e^{-(N/RT)\epsilon}\}^2}$$

and, substituting for n_0 its value given by equation (4), this gives equation (5) above.

Planck's formula can be simplified by expanding the denominator in the form of a series * ; it then becomes :

$$\checkmark \quad E_{\lambda} = hc^2\lambda^{-5} \frac{1}{1 + (Nhc/R\lambda T) - 1} = c\lambda^{-4} \frac{R}{N} T. = \frac{cKT}{\lambda^4}$$

This is the expression which had been given previously by Lord Rayleigh, and which was found to agree with experiment only at long wave-lengths for the range of temperatures available, and to show considerable divergences in the visible spectrum and in the ultra-violet. It gives $E_{\lambda} = \infty$ when λ tends to zero, and this is not in accordance with the experimental results.

For practical purposes Planck's formula may be written thus :

$$E_{\lambda} = 3.71 \times 10^{-5} \frac{\lambda^{-5}}{e^{1.435/\lambda T} - 1}.$$

It must be remembered that $E_{\lambda} \cdot \Delta\lambda$ is the quantity of radiant energy, in ergs per second, emitted by one square cm. of a perfect radiator at temperature T , within the wave-length interval defined by the limits λ and $\lambda + \Delta\lambda$.

Einstein in 1916 gave an important demonstration of Planck's formula as follows : let us suppose that in an enclosure at temperature T , containing total radiation, there is a large number of particles (molecules or atoms) each of which possesses a certain amount of internal energy at a given instant.

When this energy changes from the value E_m to a smaller value E_n the result is emission of monochromatic radiation of frequency ν , where ν is given by the general relation ; $h\nu = E_m - E_n = hc/\lambda$. (This is the law discovered by Bohr to apply to all cases in which an atomic system passes from one energy level to another, with the absorption or emission of energy ; we shall deal with it fully in Chap. II.)

When thermal equilibrium has been established, the total energy of the particles remains constant and the average number N_m of those having energy equal to E_m at any given moment can be found by Gibbs' law :

$$N_m = Ce^{-E_m/kT}$$

where C is a constant.

* When λT is large $e^{hc/k\lambda T}$ is approximately equal to $1 + hc/k\lambda T$.

The number of transfers from level E_m to E_n is clearly equal to the number of transfers in the reverse direction in the same interval of time. Now the transfer $E_m \rightarrow E_n$ which results in a *more stable* state may either take place spontaneously with a probability $A_{n,m}$ which is independent of the temperature T and *does not depend on any known cause* (as if it were a case of radioactive transformation), or it may take place under the influence of energy radiation $E_{\lambda,T}$ with a probability $B_{n,m} \cdot E_{\lambda,T}$, which is proportional to the energy density $E_{\lambda,T}$.

The transfer in the opposite direction, $E_n \rightarrow E_m$ can only take place under the influence of the radiation, the probability being $B_{m,n} \cdot E_{\lambda,T}$.

Thus in the state of equilibrium :

$$e^{-E_m/kT} \{ A_{n,m} + B_{n,m} E_{\lambda,T} \} = e^{-E_n/kT} B_{m,n} E_{\lambda,T} \quad . \quad . \quad . \quad (\alpha)$$

Remembering that $hc/\lambda = E_m - E_n$, it follows at once that

$$E_{\lambda,T} = \frac{A_{n,m}}{B_{m,n} e^{hc/k\lambda T} - B_{n,m}},$$

and since the energy $E_{\lambda,T}$ must become infinitely large as the temperature tends to infinity, it follows that $B_{m,n} = B_{n,m}$.

Hence

$$E_{\lambda,T} = \frac{A_{n,m}}{B_{m,n} (e^{hc/k\lambda T} - 1)}.$$

It is now only necessary to combine this result with that found on p. 17 regarding the form of the function $E_{\lambda,T}$, viz., $\alpha \lambda^{-5} f(\lambda T)$, and it will be seen at once that the formula must have the form :

$$E_{\lambda,T} = c_1 \frac{\lambda^{-5}}{e^{c_2/\lambda T} - 1},$$

and this is precisely the formula deduced by Planck.

The Formulæ of Rayleigh and Jeans and of Wien

Before going on to consider Planck's formula, we will discuss those of Lord Rayleigh and of Wien more fully :

Wien's law $E_{\lambda} = (hc^2/\lambda^5) e^{-ch/k\lambda T} \quad . \quad . \quad . \quad . \quad . \quad (1)$

Planck's expression reduces to this when λT is small, so that

it may be used as an approximation in the ultra-violet or at low temperatures.

If, on the other hand, λT is large, Planck's formula becomes identical with that of Rayleigh :

$$\text{Rayleigh-Jeans law} \quad E_{\lambda^*} = ckT/\lambda^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

and this can be used in the infra-red or at high temperatures.

If, now, it be remembered that the energy ΔE per cubic cm. is given by $\Delta E = (8\pi/c)E_\lambda d\lambda$ and that $\lambda = c/\nu$, it will be seen that (1) and (2) can be put into the following forms :

$$\Delta E = (8\pi\nu^2/c^3)kT d\nu \quad (\text{Lord Rayleigh}),$$

$$\Delta E = (8\pi\nu^2/c^3)h\nu e^{-h\nu/kT}d\nu \quad (\text{Wien}),$$

$$\Delta E = (8\pi\nu^2/c^3)h\nu \frac{d\nu}{e^{h\nu/kT} - 1} \quad (\text{Planck}).$$

All these expressions refer to polarised light ; for ordinary light the values must be doubled.

Let us return for a moment to the method by which Einstein obtained Planck's formula by introducing two coefficients A and B referring respectively to the probability of spontaneous and of induced changes ; whilst the latter type of change belongs to the *classical* system, in that it corresponds to the old conception of an oscillator acted upon by electromagnetic waves, the idea of a spontaneous change is new, in that it contemplates emission which does not depend on any known cause, as in the case of radioactive phenomena ; it is easy to show that the coefficient B is connected with the *undulatory* character of the radiation and that A is connected with its *corpuscular* character. Actually, if A tends to zero it means that the conditions being considered are those in which λ is large, *i.e.*, those to which Rayleigh's formula applies ; this formula expresses the undulatory nature of light and is obtained by purely classical reasoning (see p. 160). If, however, B tends to zero, it means that the conditions are those of low temperature or high frequency, for equation (α) gives $e^{-c^2 h / k \lambda T} A_{n, m} \simeq 0$, and then Wien's formula applies ; this formula is obtained by reasoning from the corpuscular theory of radiation (see p. 215).

From this point onwards the idea of a dual character of radiation takes shape and we shall develop it more fully in Chap. VI.

The Measurement of Energy

In practice the intensities of the monochromatic radiations in the spectrum are measured by means of the bolometer invented by Langley. It consists of a very fine platinum wire blackened on the surface and forming part of an electric circuit or, better, one arm of a Wheatstone bridge in which a very delicate galvanometer is inserted. On account of the surface blackening, the filament absorbs practically all the energy that falls on it and transforms this into heat with the result that the temperature of the filament rises and hence also its electrical resistance; this increase of resistance can be measured with very high precision by means of a Wheatstone bridge, and hence the temperature of the filament may be found to a millionth of a degree centigrade.

The energy distribution in the various parts of the solar spectrum has been studied experimentally in this way, and it has been found that this distribution differs very little from that of a black body at a temperature of about $6,000^{\circ}$.

In stellar astronomy the bolometer has been used especially for measuring the total energy which a star radiates to the telescope objective; this is obtained by placing a blackened disc at the position of the point image of the star formed at the focus of the instrument.

Similar measurements can be made with the thermopile or with a Nichols' radiometer.

The former of these instruments is based, as will be remembered, on Seebeck's discovery that if a closed metallic circuit be formed of two different metals, the application of heat to one of the junctions generates an electric current in the circuit. Nobili made use of this fact in constructing his thermopile which was composed of a number of couples, each consisting of a rod of bismuth and one of antimony.

For measuring stellar radiation the simple bismuth-platinum thermocouple, due to Coblentz, is used; the junction of the two wires is attached to a small *receiving* disc placed so that the focal image of the star formed at the focus of a large telescope falls upon the disc. Coblentz succeeded in measuring the radiant energy from a sixth magnitude star; he deduced that, while the solar radiation on a square cm. of the earth's surface is about 2 gram-calories per minute, the radiation from all the stars, taken together, is about 1 gram-calorie per century.

Nichols' radiometer (1906) consists of a hollow box ($10 \times 5 \times 5$ cm.) inside which there is a fine quartz thread some thousandths of a millimetre in diameter, which acts as a suspension for a horizontal arm carrying at either end a blackened mica disc, 2 mm. in diameter.

Attached to the lower end of the quartz is a tiny mirror which reflects a beam of light on to a graduated scale and so indicates the extent to which the arm is rotated. The interior of the box is evacuated and the light to be measured (*e.g.*, that emitted by a star) passes through a heat-transparent fluorite window and falls on to one of the mica discs. The pressure of the radiant energy causes the thread to twist, and the consequent rotation of the mirror causes the beam of light serving as an indicator to move across the graduated scale.

The apparatus is calibrated by means of an artificial source.

The instruments which we have just described are sensitive to *all radiations* and so measure the total energy contained in the radiation; the human eye and the photographic plate, on the other hand, are selective since they are only sensitive to a certain range of wave-lengths.

The Connection between Avogadro's Number and Planck's Constant

One application of Planck's formula is to the determination of Avogadro's number, N , from a knowledge of the energy intensity corresponding to a given wave-length; at the same time, Planck's constant can be found: for this purpose it is sufficient to know two values of λ and the two corresponding values of E_{λ} .

This calculation can be made without repeating the measurements of the intensity (E_{λ}), the temperature and the

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wave-length, if we make use of two figures which are already very accurately known, viz., Wien's constant ($\lambda_m T = 0.288$) and Stefan's constant which appears in the important equation $W = \sigma T^4$. The value of σ is known to be 5.7×10^{-5} .

The calculation can be carried out as follows :

The value of the quantity $2 \int_0^\infty E_\lambda d\lambda$ is found by integrating Planck's formula ; this gives

$$2 \int_0^\infty E_\lambda d\lambda = 13 \frac{R^4}{N^4 h^3 c^2} T^4.$$

This expression can easily be equated to an expression for $2 \int_0^\infty E_\lambda d\lambda$ which occurs in the development of Stefan's law * :

* The calculation referred to is as follows :—

It was found on p. 9 that the total energy density in a closed space was

$$U = (8\pi/c) \int_0^\infty E_\lambda d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

and on p. 12 it was shown that

$$U = aT^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Hence

$$2 \int_0^\infty E_\lambda d\lambda = a(c/4\pi)T^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Now, for a point on the surface of a black-body, if we consider an elementary cone of aperture $d\omega$ and an element of surface whose area (projected on a plane normal to the axis of the cone) is dS , the energy radiated per second within the cone is

$$W = 2dS \cdot d\omega \int_0^\infty E_\lambda d\lambda \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Integrating twice, we obtain the value of the energy radiated per sq. cm. in all directions

$$W = a(c/4)T^4 = \sigma T^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Finally, developing Planck's formula in series to find $\int_0^\infty E_\lambda d\lambda$, we obtain

$$2 \int_0^\infty E_\lambda d\lambda = 13 \frac{R^4}{h^3 c^2 N^4} T^4 = \frac{\sigma}{\pi} T^4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

This gives

$$\sigma = \frac{2\pi^5 k^4}{15c^2 h^3} = 5.72 \times 10^{-5} \text{ erg cm.}^{-2} \text{ deg.}^{-4} \text{ sec.}^{-1} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

$$\text{i.e., approximately,} \quad \sigma = \frac{13\pi R^4}{h^3 c^2 N^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

since $k \equiv R/N$ and $2\pi^4/15 = 13$ very nearly.

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the result obtained is

$$h^3 N^4 = (1/\sigma) 21.5 \times 10^{11},$$

where σ is Stefan's constant.

Finally, if Planck's formula be differentiated with respect to λ and the result equated to zero, we find the value of λ_m , the point corresponding to the peak of the bell-shaped curve; a simple calculation, putting $\lambda_m T$ equal to 0.288, the value of Wien's constant, gives the expression

$$\frac{N}{R} \frac{hc}{\lambda_m T} = 4.96 \quad \text{or} \quad hN \cong 0.004.$$

Thus we have the two equations

$$h^3 N^4 = 3.78 \times 10^{16}$$

$$h N = 0.004$$

containing as unknowns the two quantities h (Planck's constant) and N (Avogadro's number); solving these equations we find

$$h = 6.55 \times 10^{-27} \quad N = 60 \times 10^{22}.$$

Avogadro's number is thus found once again and the new figure agrees with the values previously obtained, not simply as regards order of magnitude but absolutely; this provides a confirmation of the exactness of Planck's theory.

Planck's bold hypothesis, deduced by an involved process of reasoning from statistics and thermodynamics, received very careful consideration at the hands of the more enlightened physicists, the more profound thinkers of the time; nevertheless in spite of the support of men like Einstein and Poincaré, it would probably have been relegated to the philosophy of physics and buried for all practical purposes, if certain experimenters had not been led to examine other phenomena, more simple and less abstruse, which indicated the existence of a discontinuity in nature which, until then, had been entirely unsuspected. While Planck in 1900 had simply asserted that the electrons emitted and absorbed energy in fixed finite quantities and shortly afterwards revised this new conception by restricting it to the process of emission, Einstein, in 1905, daringly proposed the theory that these fixed and finite quantities of radiant energy retained their

separate identities throughout their journey from the instant of emission to the instant of absorption. In Chap. VI we shall examine this reasoning, but for the present we shall confine ourselves to mentioning the fact that the latest developments of physics have confirmed the idea that in all *elementary* phenomena, *i.e.*, those which concern a single atom, a single molecule, or a single electron, the discontinuity postulated by Planck is found to exist; in such elementary phenomena Nature proceeds by jumps, or degrees; in macroscopic phenomena this discontinuity is hidden and it remained unsuspected by physicists for centuries.

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CHAPTER II

SPECTROSCOPY, BOHR'S THEORY AND THE ENERGY LEVELS OF THE ATOM

Spectroscopy and Science

TOWARDS the middle of the last century spectroscopy began to be of importance in the analysis of the elements and in astrophysics, and became a field of investigation of sufficient importance to constitute a separate science. An enormous mass of material had been accumulated which, although admittedly empirical, represented, from the point of view of the precision and the nicety of the measurements, perfect data. This material seemed however to resist every attempt made to adduce some common criterion of order in the multiplicity of number and character of the spectral lines. Thus at the end of the century, after Zeeman had contributed the important discovery bearing his name (of which we shall speak later), spectroscopy, despite its many successful applications, remained an empirical science almost completely detached from the theories which served to co-ordinate other branches of physics.

However, Balmer, Rydberg, Ritz and others were successful in establishing certain regularities in the spectrum of a given element and relations both quantitative and qualitative between the spectra of different elements.

As basis, certain laws were formulated which served as guiding principles in disentangling the complicated network of the spectral lines, which for some substances number many hundreds. It was found, for example, that a series of lines given by hydrogen responded to the simple formula $\nu = R \left(\frac{1}{2^2} - \frac{1}{n^2} \right) *$ and the result

* R is a constant ; n denotes the series of integers 3, 4, 5, 6 . .

emerged, that very frequently a line is related to others by the relation $\nu = \nu_1 + \nu_2$, *i.e.*, an observed frequency is the sum of two other observed frequencies.

In the present century, by the aid of the quantum theory and the Rutherford model of the atom, happily combined by Bohr, all the phenomena of spectra were attacked at their source, the known facts were explained and fresh ones brought to light.

Thanks to the patient endeavours of the specialists, the laws of experimental spectroscopy have practically reached their definitive formulation, and a high degree of refinement in technical applications has resulted. At the same time theories have been elaborated, based on this observational groundwork, which aim at explaining the intimate constitution of matter.

The history of this branch of physics prompts a reflection which is, at once, both gratifying and discouraging. The first observations, the first facts ascertained, are the most salient, but after these follow other subtler and less obvious discoveries. The simple models first devised to co-ordinate and explain the facts are then seen to be incapable of incorporating into a coherent theory the mass of material brought to light. By using spectrometers of higher resolving power, spectral lines were found to be complex and recourse had to be had to relativity. It was observed that certain lines consisted of groups of closely spaced components. This required an explanation. Zeeman discovered the effect of a magnetic field. At first the simple effect was observed, and the phenomenon was interpreted, but almost immediately afterwards more complicated aspects were brought to light, and it was necessary to introduce the theory of the rotating electron, the correctness of which has since been established by evidence from other directions. Finally, quantum mechanics emerged revealing a new and unforeseen physics holding sway in the domain of the atom.

Such are the vicissitudes of human knowledge. The scientific horizon recedes before the scientist's scrutiny, and we are tempted to speculate on the value of science and to wonder what its destiny may be. There is no respite, no natural limit where our efforts can be relaxed. But a world with no future, without innovation,

with nothing to discover and to hope for, would be a sorry place. A generation born into a universe where human knowledge has attained to an apparent finality stands in need of new life and of rejuvenescence. There will be no mourning for a theory which is submerged if another more vital and more general theory rises to replace it. (Clairaut (1713–1765), on learning that Newton had discovered the law of universal gravitation and the infinitesimal calculus with which the consequences of the law could be worked out, expressed regret that astronomy would then have nothing to do !)

Niels Bohr, with whose work we shall, in the main, be concerned in this chapter, is not one of those specialists who multiply experiments in a small field without regard to the close relations between the different branches of science. He possesses in high degree the research spirit, coupled with a mental audacity which has enabled him to throw off the old methods and worn-out conceptions, to find new approaches to a higher and more general view of phenomena. The experimental facts themselves are of course indispensable to the progress of science. They may in fact be regarded as the bony skeleton which resists the test of time. But, in the face of the mass and variety of observed phenomena, the intelligence would be overwhelmed and science would crack under the weight of material if it were not for the appearance from time to time, of a bold innovator with the theory which will harmonise and regroup the facts of experiment and predict new phenomena.

To return to spectroscopy, spectra, as already pointed out in Vol. I, Chap. II, are of two kinds, *absorption* and *emission spectra*. These include :

(α) *Line spectra*, composed of separate lines, which are distinguished as “primary” or flame spectra, when the emitting atom is the neutral atom; secondary or spark spectra if the atom is simply ionised, *i.e.*, lacks an electron. There are also spectra of higher orders produced by atoms which have lost two, three or more electrons.

(β) *Band spectra*, also made up of lines, but in general more closely

spaced, and converging on certain limiting frequencies. Band spectra originate from molecules.

(γ) *continuous spectra*, (black body radiation, general X-radiation).

In physical laboratories emission spectra are obtained using a flame, the electric arc or electric spark. In general the arc spectrum differs from the flame spectrum merely by the presence of a certain number of additional lines. In passing from the arc to the spark spectrum not only do new lines appear but many existing lines are intensified, others becoming weaker and some vanishing altogether.

The lines which are reinforced are due to *ionised atoms*, that is, to atoms which have lost an electron because of the powerful excitation of the spark, and are the lines which Lockyer called *enhanced lines*. He thought that in the heat of the spark the "element" might be decomposed into a simpler element. Actually the new "element" is the ion. The atom can be ionised once or it may be doubly ionised, triply ionised and so on. In each state of ionisation it emits a characteristic spectrum.

These spectra are of immense importance in the study of the stars. They appear in the various species of *spectral classes* presented by the stars corresponding to their different temperatures. The degree of ionisation of a gas (the fraction of the atoms which have lost one or more electrons) depends not only on the temperature but also on the pressure. The theory worked out by Saha to take account of this effect is successfully applied in the spectroscopic investigation of the stars.

It may be mentioned here, in passing, that Bowen (1927) has discovered that certain lines (λ 3726.16 for example), which appear strongly in the spectra of gaseous nebulae, are due to ionised oxygen or ionised nitrogen, whereas it had always been believed that they indicated the existence of an element, unknown on the earth and in the other celestial bodies, to which the name *nebulium* had been given.

The characteristics of the spectrum, that is, the splitting up and coalescence of certain lines, the appearance of other normally

“ forbidden ” lines, etc., are controlled by the external conditions under which the change of state of the emitting atom occurs, in particular by the presence of (1) an electric field (Stark-Lo Surdo effect); (2) a weak or strong magnetic field (Zeeman effect, Paschen-Back effect); (3) thermal motion (Doppler effect).

In addition, spectroscopy has to occupy itself with the study of the polarisation of the emitted or absorbed light, the intensities of the spectral lines, the durations of the absorption and emission processes, the permanence of the excited states from which lines originate, etc.

In this colossal field* the experimental data have been systematised and brought to a high degree of perfection in the course of a few years. On the theoretical side a great deal has been accomplished, and something of this will be discussed later. We may mention—to give a preliminary idea—that for some elements, such as hydrogen and helium, the theory has enabled all the frequencies of the entire spectrum to be calculated in terms of universal constants only, (mass of the electron, the electronic charge, the quantum constant). The theoretical predictions are in such complete accord with experiment that if the calculated spectrum were traced on a photographic plate, and the plate then inserted in the spectrograph and the actual spectrum of the element photographed to the same scale, perfect superposition of the two images, line for line, would be obtained.

With the same marvellous precision, the developments of the quantum theory foretell the modifications which these spectra undergo in an electric field (Stark-Lo Surdo effect) or in a magnetic field (Zeeman effect).

With the concepts of classical physics it was impossible to devise a mechanism composed of electrons and positive charges, capable of yielding the vibrations revealed by spectra. In this the quantum theory succeeded. Moreover, in the process, a common architecture for all the atoms was discovered and a new mechanics of the atom developed.

* Among the earlier spectroscopic researches may be mentioned those of Balmer, Rydberg, Ritz, Runge. Recent work is due in particular to Bohr, Sommerfeld, Russell, Saunders, Landé, Heisenberg, Hund, Pauli, Uhlenbeck, Goudsmit, Kramers, Bowen, Paschen, Fowler, Grotrian and others.

Bohr's Postulates and their First Applications

In 1913, a young Danish physicist brought to the notice of an astonished world a simple theory which, linking itself closely with Planck's ideas and introducing the quantum of action discovered by Planck, accounted perfectly for the lines of the hydrogen spectrum. To the admiration demanded by a discovery of such importance was added that aroused by the youth of the author who was then only twenty-seven years old.

Bohr's investigation led to so simple and precise an explanation of spectroscopic data, and to so clear a picture of the structure of atoms and of the periodicity in their physical and chemical properties, that it may be considered as the point of departure of a new era in atomic physics and in chemistry.

The remarkable advances due to Bohr and his school were pursued and extended by a host of other physicists, particularly German physicists, among whom we may mention Sommerfeld, Epstein, Pauli, Landé, Heisenberg, Hund, Born, etc. Thus, in the course of fifteen years a theoretical structure has been erected co-ordinating an imposing array of experimental phenomena, such as the emission of spectral lines, the emission of molecular spectra, X-ray spectra, the Zeeman, Stark, Raman and Compton effects, atomic magnetism, periodic structure of the elements, etc., etc.

The persistent efforts of physicists to arrive at an understanding of the process of emission of spectral lines were justified by the great importance of the problem in the theory of the constitution of matter. Moreover, spectroscopy had attained to such a degree of perfection and utility that the question was a burning one. Bohr commenced by explaining in fundamental terms, how the spectral lines arise in the case of hydrogen.

It was realised that the Rutherford atom would be an unstable system if the external electrons were to emit energy in their motion, as required by classical electrodynamics. In particular, the hydrogen atom, comprising a nucleus (the proton), about which revolved a single electron in a circular or elliptical orbit, would emit continuously waves of frequency equal to that of the orbital motion, and there would be a steady emission of energy.

Actually the atom is a stationary system which normally does not radiate.

Clearly a new conception was required. It became necessary to assume the atom to be a mechanism in which the electrons rotate in orbits in a stationary or unchanging *régime*, without emitting radiation. The laws of electrodynamics, acknowledged to be true for energy when propagated, were thus shown to be inapplicable to the motion of a single electron, and Bohr enunciated his first postulate, that an electron, describing a circle or ellipse about the nucleus of an atom, does not radiate.

Under what conditions, then, does the atom radiate? What is the connection between the radiator and the radiation?

We begin by considering an example already met with, the relation between cathode rays and the X-rays to which they give rise. As pointed out, these X-rays are formed when a stream of cathode particles impinges on to the anticathode. The wave-length of the X-rays emitted can be measured by means of crystals. Analysis of the X-radiation proceeding from the anticathode shows that there are present rays of all frequencies up to a certain well-defined maximum frequency, the value of which depends only on the potential applied to the discharge tube. At this critical frequency all radiation ceases absolutely; the spectrum is truncated. If V is the potential applied to the tube, the kinetic energy of an electron striking the anticathode is given by $Ve = \frac{1}{2}mv^2$, and it is found that the maximum frequency of X-radiation emitted is related to the potential V by the formula $Ve = h\nu$, where h is a numerical constant, independent not only of ν but also of the type of tube and the metals forming cathode and anticathode.

The value of h as previously mentioned in Vol. I., p. 238, is

$$h = 6.55 \times 10^{-27} \text{ erg} \times \text{sec.}$$

Suppose X-radiation, say, of frequency equal to the critical frequency $\nu_{\text{max.}}$, is allowed to fall on some solid substance. The X-rays will be absorbed to a greater or less extent, and electrons will be emitted by the substance. The velocities of these electrons can be measured by methods indicated previously. It is found

that the maximum velocity of these secondary electrons ejected by X-rays of frequency $\nu_{\text{max.}}$, exactly equals that of the primary cathode stream electrons which gave rise to the X-rays. Thus the kinetic energy of the expelled electron is related to the X-ray frequency by the same equation, $\frac{1}{2}mv^2 = h\nu$, as connects the X-ray frequency with the energy of the primary cathode particle. This result will be re-examined more fully in Chapter V.

To sum up, the equation $\frac{1}{2}mv^2 = h\nu$, read from left to right, corresponds to the formation of the X-ray spectrum. Read from right to left, it interprets the inverse phenomenon. It is clearly evident from the preceding discussion, that this factor h is of the greatest importance in the reciprocal exchanges of energy between the electron and electromagnetic radiation. Planck had already been forced to the, at first sight, disconcerting conclusion that the atom emits and absorbs energy, only in discrete "quanta" of amount $h\nu$ and never in small fractions. Bohr regarded the atom as a mechanism in which the different electrons occupied certain stationary orbits, the only ones possible for dynamical equilibrium, moving round in these orbits without emitting energy. In the abrupt passage from one orbit to another (each orbit corresponding to an energy level W), an electron was assumed to emit monochromatic radiation of frequency ν , defined by the formula :

$$\text{frequency} = \frac{\text{difference of energy}}{h} \quad \text{or} \quad \nu = \frac{W_1 - W_2}{h}$$

The close connection between this second postulate of Bohr and the theory put forward by Planck will be immediately obvious when it is recalled that Planck took as the fundamental assumption of his theory, the formula $W = nh\nu$, affirming that the energy of an oscillator could assume only certain multiples of the unit $h\nu$.

Bohr's third postulate affirmed that in each possible orbit of an electron, the conditions of dynamical equilibrium were determined by classical mechanics. This means, in other words, that, in the case of hydrogen, the nucleus attracts the encircling electron with a force subject to Coulomb's law and the electron is prevented from falling into the nucleus because its centrifugal

force equals this attraction. The question which here suggests itself even to a non-mathematical mind is, how, in the case of an atom having a swarm of 30, 40, or more (up to 92) electrons whirling round the central nucleus, is it possible to calculate the energy of the system and from this the frequency emitted in the passage between two states W_1 and W_2 ?

This problem, it may be admitted at once, has not been solved except for the simplest atom, hydrogen, and at length after laborious attempts to perform the calculations, the search for the solution for the other more complex atoms has been abandoned. We shall refer to this later.

Not even for helium, the atom of which contains only two peripheral electrons, has the problem been solved. But the impossibility is not merely a mathematical one. It has a more fundamental origin in the basic conception or model. It is due to the fact that the atom is not subject to ordinary, so-called classical, mechanics.

We find ourselves in possession of an atomic model, and we shall see how far the theory put forward by the great Danish scientist and generalised by Sommerfeld, is able to take us. This theory has in fact rendered invaluable service, even though to-day it has become necessary to abandon the notion of orbits. Much remains of the ingenious superstructure based on the theory by the unremitting labours of Bohr in the years prior to 1924.

The reader need not be perplexed by the first postulate. The foundations of the electromagnetic theory are not here being attacked. It is simply the assumption of a mechanical model to interpret a phenomenon connected with radiation. The unquestionable effect observed is that a simple radiation appears as the result of the difference $(E_1 - E_2)$ of two energy states of the atom, and more precisely, the frequency emitted is given

by $\nu = \frac{1}{h} (E_1 - E_2)$. We proceed to investigate these energy states and to express them in terms of the physical constants already mentioned, mass and charge of the electron, Planck's constant, etc.

How the experimental determination of the different energy states has been accomplished will be explained later.

After this general discussion, we pass immediately to the calculation of the orbits for an atom consisting of a nucleus of charge e and a single electron gravitating round the nucleus in a circular orbit, like a planet encircling the sun. Only the hydrogen atom, consisting of a singly charged central *proton* and one electron, will correspond to this case. We shall consider, however, the more general system in which the central charge is Ze , i.e., an integral multiple of e . This case will include any atom with electrons, all but one of which have been expelled. For an orbit of arbitrary radius r , the following equation expressing the equality of the centrifugal force $\frac{mv^2}{r}$ and the Coulombian attraction, holds good :

$$\frac{mv^2}{r} = \frac{Ze^2}{r^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The kinetic energy of an electron is given by $\frac{1}{2}mv^2 = \frac{Ze^2}{2r}$. The potential energy * is known to be $-\frac{Ze^2}{r}$ and the total energy W becomes

$$W = \frac{Ze^2}{2r} - \frac{Ze^2}{r} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Actually the potential energy must, as usual, involve an additive constant, but since we consider only *differences* between the different energy states, it serves no useful purpose to introduce the constant, just as in dealing with water falling from one level to another in a hydroelectric installation, it serves no useful purpose to consider the absolute heights above sea level of the upper and lower points of the conduit. It is their difference which is of importance.

* This has negative sign because, owing to the attraction between nucleus and electron, an *increase* in the distance r implies an *increase* in the potential energy. As the latter is *inversely* proportional to r , it can only increase with r if the negative sign is prefixed.

The total amount of energy concerned in the phenomenon considered, the passage of an electron from one orbit to another, is therefore $W = -\frac{Ze^2}{2r}$.

Up to this point use has been made only of the laws of classical mechanics in obtaining the relations (1) and (2). It will be impossible, however, with the help of these laws alone, to determine the orbits or, to be exact, the discrete series of orbits, which the electron will occupy. To do this recourse must be had to the concept of discontinuity embodied in the doctrine of quanta.

The relation introduced by Bohr to express this discontinuity, or stepwise variation of the energy, was the following :

$$mv \times 2\pi r = nh \quad \text{with } n = 1, 2, 3, 4 \dots \dots (3)$$

which states that the product of the impulse mv into the length of the orbit can assume only such values as are integral multiples of the quantum of action h .

From this relation, we derive at once a step by step variation of the energy and of the orbital radius. The latter in fact can only assume one of the following discrete series of values :

$$\text{radius of the circular orbit } r = \frac{n^2 h^2}{4\pi^2 m Z e^2} \dots \dots (4)$$

a result following easily from (1), (2) and (3). The energy possessed by the electron in an orbit defined by the number n is expressed by :

$$\begin{array}{l} \text{energy of the orbit} \\ \text{of quantum number } n \end{array} \quad W = -\frac{2\pi^2 m Z^2 e^4}{n^2 h^2} \dots \dots (5)$$

Thus, introducing Bohr's second postulate, the frequency emitted by a single electron atom when the electron passes from one stationary orbit to another, owing to any cause whatever, will be given by :

frequency emitted in the transition between two orbits

$$\nu = \frac{\Delta W}{h} = \frac{2\pi^2 m e^4 Z^2}{h^3} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \dots \dots (6)$$

For the hydrogen atom $Z = 1$ and all possible lines of its spectrum are expressed in the formula :

$$\nu = \frac{2\pi^2me^4}{h^3} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \quad . \quad . \quad . \quad . \quad . \quad (6^1)$$

For the sake of clearness, it may be pointed out that n_2 is the ordinal number of the initial orbit, n_1 that of the final orbit. Emission occurs when the electron changes orbit, passing from the outside towards the inside. To the inside orbit corresponds the smaller quantum number n_1 . In the reverse transition, on the other hand, absorption of energy takes place. To pass to the most distant orbit, that is, to escape from the nucleus, the electron will require the maximum energy, and in that case the atom becomes *ionised*, *i.e.*, loses an electron.

The deductions made on the assumption of a single electron attracted towards a central charge, hold both for the hydrogen atom and for the helium atom which has become ionised by the loss of one of its electrons.

The results will still hold good, as approximations, for atoms having a single electron situated far out in the periphery so that the nucleus, which attracts, and the electrons in its vicinity, which repel, can be regarded as together forming a simple attracting centre. This point will be better understood in the sequel.

The Atom of Hydrogen and its Spectrum

Bohr's theory predicts that the hydrogen spectrum will consist of lines whose frequencies are given by the following formula :

$$\nu = \frac{2\pi^2me^4}{h^3} \left\{ \frac{1}{n_1^2} - \frac{1}{n_2^2} \right\} \quad . \quad . \quad . \quad . \quad . \quad (6')^*$$

* Note that the frequencies of spectral lines are not measurable directly. What is actually measured is the wave-length of any simple radiation, expressed in microns, millimicrons (10^{-7} cm.), Ångström units (10^{-8} cm.) or X-ray units (10^{-11} cm.), according to the order of magnitude. The reciprocal $\frac{1}{\lambda}$ represents the number of wave-lengths contained in a centimetre and is termed the *wave number*. The frequency ν is the product of the wave number $\frac{1}{\lambda}$ and the velocity of light c . As, however, c is known only approximately (to about one part in a thousand) the derived frequencies are less exact than the

In 1885 the Swiss physicist Balmer had identified in the hydrogen spectrum a series of lines extending from the red to the ultra-violet, the frequencies of which obeyed the following empirical law :

$$\text{Balmer series} \quad \nu = \nu_0 \left(\frac{1}{2^2} - \frac{1}{n^2} \right) \quad \text{With } n = 3, 4, 5, 6 \quad . \quad (7)$$

ν_0 being a constant with the value 329033×10^{10} .

It is immediately obvious that this series of Balmer's is only a special case of Bohr's general expression with n_1 put equal to 2,

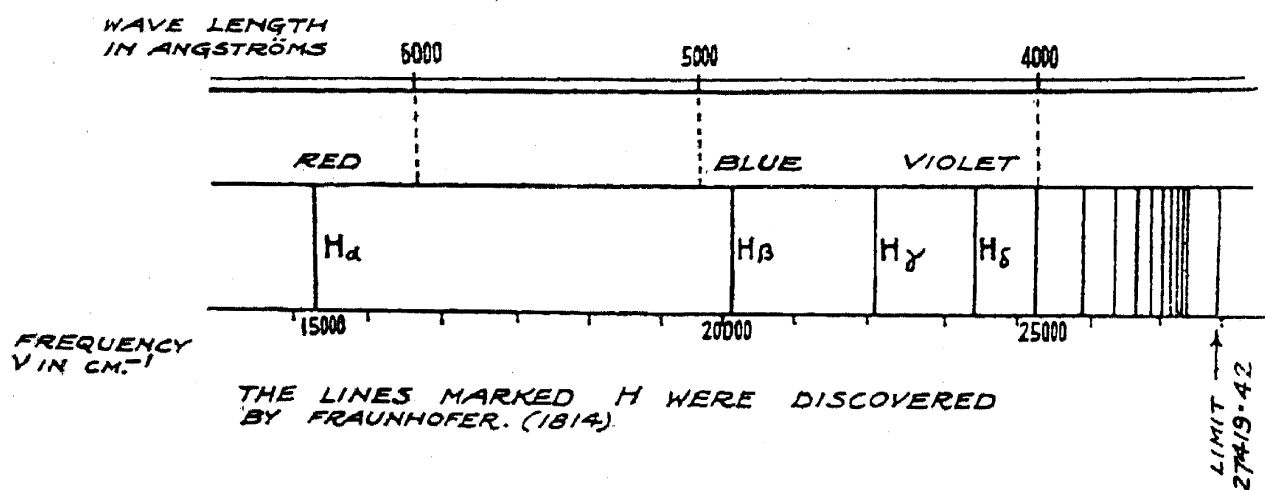


FIG. 3.—The spectrum of hydrogen.

or, in other words, when electron transitions from various orbits to the final orbit $n_1 = 2$ are considered.

Another series in the spectrum of hydrogen, situated in the infra-red, was discovered in 1909 by Paschen and appropriately

measured wave-lengths, and it is preferable to employ the latter or, better still, their reciprocals, the wave numbers. The formula giving the various series of the hydrogen spectrum then runs :

$$\frac{1}{\lambda} = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

The constant R , which is of immense importance in this discussion, has the value 109678, and is known as Rydberg's constant. The accuracy with which the formula fits the observational data is shown by comparison of the wave numbers of the first six members of the Balmer series, (a) as computed from the formula, (b) as obtained experimentally.

Wave numbers of the first six lines of the Balmer series

(a) Computed	15233.17	20564.77	23032.54	24373.06	25181.35	25705.97
(b) Observed.	15233.22	20564.79	23032.54	24373.06	25181.34	25705.96

In obtaining the computed values R was put equal to 109678.8.

bears his name. The lines of the series conformed to the following law :

$$\text{Paschen series} \quad \nu = \nu_0 \left(\frac{1}{3^2} - \frac{1}{n^2} \right) \quad \text{With } n = 4, 5, 6 \quad . \quad . \quad (8)$$

Finally, another physicist, Lyman (1914), observed in the ultra-violet certain lines which fitted the formula :

$$\text{Lyman series} \quad \nu = \nu_0 \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad \text{With } n = 2, 3, 4 \quad . \quad . \quad (9)$$

These relations, like Balmer's, represent special cases of Bohr's formula. Moreover, Bohr's constant, $\frac{2\pi^2me^4}{h^3}$, occurring in (6), when evaluated, using the well-known values of h , m , e , comes out exactly equal to the coefficient ν_0 , which appears in the series formulæ of Balmer, Paschen and Lyman, and which had already been found empirically. It is only necessary to substitute in $\frac{2\pi^2me^4}{h^3}$, the values $e = 4.77 \times 10^{-10}$, $\frac{e}{m} = 5.31 \times 10^{17}$, and $h = 6.55 \times 10^{-27}$, to verify this relation.

Of the Balmer series, represented by the formula $\nu = \nu_0 \left(\frac{1}{4} - \frac{1}{n^2} \right)$, the first 20 lines have been observed in Geissler tubes and a further 13 lines in the spectra of nebulae where matter is in an even more tenuous state than in the highest "vacuum" of the Geissler tube.

In 1922, Brackett discovered in the infra-red, the first two lines of the series arising from electron transitions to the orbit with quantum number $n = 4$.

In normal conditions of the atom, the electron occupies the orbit nearest to the nucleus, that is, the smallest orbit. For emission of light to occur the electron must first be projected by some external influence (collision, absorption of radiational energy), on to one of the outer circles, from which it can fall back to the single quantum orbit emitting radiation in the process. From formula (4) can be calculated the radius of the single quantum orbit, or, in other words, the radius of the normal atom of hydrogen. Putting

$n = Z = 1$ and substituting the numerical values of h , m and e , the formula gives :

$$\text{radius of the hydrogen atom } r = 0.53 \times 10^{-8} \text{ cm.}$$

Thus the diameter of the atom is about 10^{-8} cm., a value which agrees with those furnished by the kinetic theory of gases and the study of crystal structure. This agreement is very satisfactory.

The radii of the different orbits increase in proportion to the

squares of their ordinal or quantum numbers. Thus, for example, the radius of the thirteenth circle equals 90×10^{-8} cm. Now, under atmospheric pressure, and at normal temperature, the average distance apart of the molecules of a gas is in the neighbourhood of 16×10^{-8} cm. It is readily realised therefore why at ordinary pressures the spectrum of hydrogen contains only the first few lines of the Balmer series.

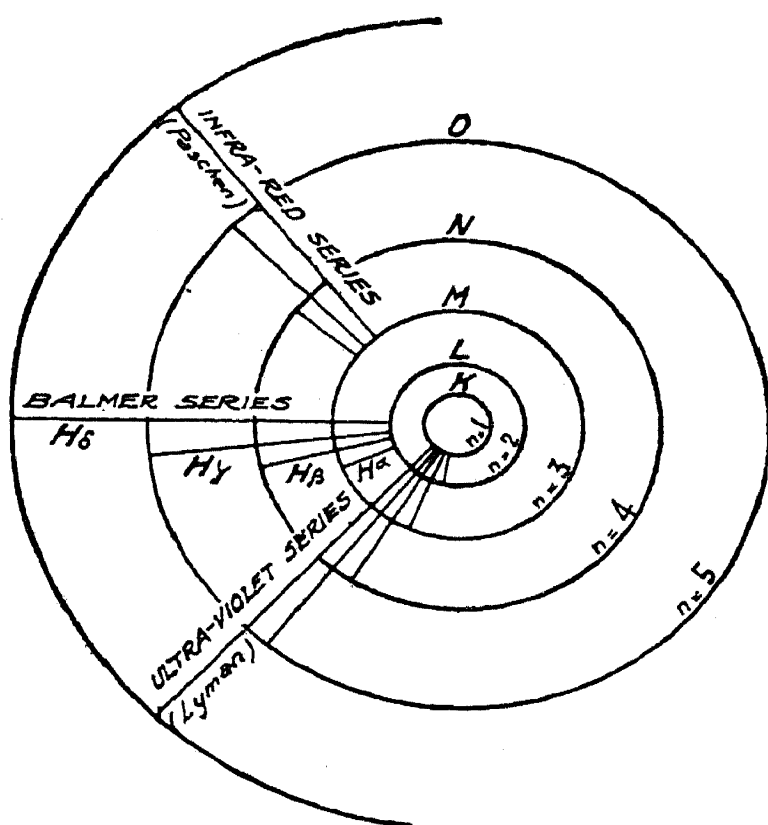


FIG. 4.

It is quite easy to calculate the electron velocity

and the time taken to describe a complete revolution.

The attention of the reader is now drawn to an important point. The details of the motion of the electron are not required for the interpretation of the spectral lines. These follow directly from the postulate that in the passage of the electron from one *energy level* to another, there is emission of monochromatic light of frequency,

$$\nu = \frac{\Delta W}{h}.$$

As will be seen more clearly in the sequel, it is the energy levels which have real existence and which are determinable directly from experiment. The “tangible” concepts in Bohr’s theory are neither the orbits nor the periods of rotation, but the energy levels, the wave-lengths of the radiations emitted and the intensities of the different lines, these intensities depending on transition probabilities. The essential fact divested of all attempts at interpretation, is the following, which should be carefully noted.

The frequency of any line whatever in the spectrum of an element is obtained by taking the difference of two numbers selected from a table of numbers characteristic of the element in question. We may add, anticipating the data which will be given, that this table contains simply the values of $\frac{W}{h}$, the energies of the atom in its different states, divided by Planck’s constant.

Thus the energy of an atom cannot decrease or increase continuously, but only by discrete steps. We shall see how direct experiments confirm that these levels, these characteristic numbers, the differences of which yield the frequencies emitted, are actually *energy levels*.

Finally we note that the energy of the hydrogen atom in its normal state is given by

$$W = - \frac{2\pi^2 me^4}{h^2},$$

and putting $R = \frac{2\pi^2 me^4}{h^3}$, we have $Rh = W$. Rh should correspond to the energy required to ionise the hydrogen atom. Carrying out the numerical calculation we find that,

$$Rh = 21.5 \times 10^{-12} \text{ erg, or } 13.5 \text{ volts,}$$

which is in agreement with experiment (see Fig. 10).

The Spectrum of Ionised Helium

The hydrogen atom, with its single electron, is the only *atom* satisfying strictly the conditions of the problem solved by Bohr. The helium *ion*, however, formed from the helium atom by the

loss of one of its two external electrons, consists like the hydrogen atom, of a positive nucleus about which a single electron rotates. It is to be expected therefore that in the spectrum of ionised helium there will occur series of lines represented by the formula :

$$\nu = 4\nu_0 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right).$$

This result is derived from equation (6) by putting $Z = 2$. This prediction has in fact been verified. The series in question have been recognised and are known as the Fowler and Pickering series respectively.*

The factor ν_0 appearing in these series is the same as that figuring in the hydrogen series. This remarkable experimental agreement between the anticipations of theory and the experimental results of spectroscopy, represents one of the principal verifications of Bohr's ideas and, at the same time, provides an irrefutable proof that the charge of the atomic nucleus of helium is double that of hydrogen.

Motion of the Nucleus

It has just been stated that values of the coefficient ν_0 appropriate respectively to the helium ion spectrum and the hydrogen spectrum, agree. Careful examination showed, however, that the agreement was not perfect. For helium ν_0 equals 329166×10^{10} , whilst its value for hydrogen is 329033×10^{10} . Bohr's theory provided a complete explanation of this difference, which is due to the motion of the nucleus. This was another success for Bohr's theory.

We shall give the detailed explanation. In developing the above theory leading to the determination of the stationary orbits, it was supposed that the nucleus remained immovable, that is, it was assumed by implication that its mass was infinite. In reality this is not the case. For hydrogen the nuclear mass is 1,840 times that of the electron, but it is not infinitely greater. It follows that whilst the planet m , that is, the electron, rotates in an orbit

* Fowler's series is obtained by putting $n_1 = 3$, Pickering's by putting $n_1 = 4$.

of radius A , the sun, S , must also rotate. It will in fact describe a circular orbit of radius a such that the centre of gravity of the system formed by the two bodies remains stationary at O . A simple theorem on centres of gravity yields the value of the radius a , which must satisfy :

$$aM = Am \quad . \quad . \quad (1)$$

To determine the stationary orbits, the same method must be followed as in the simpler case already dealt with.

If ω is the angular velocity of the planet and the sun, the equality of the centrifugal force and the attractive force between the two masses leads to the equations

$$\left. \begin{aligned} mA\omega^2 &= \frac{eE}{(a + A)^2} & e &= \text{electronic charge} \\ Ma\omega^2 &= \frac{eE}{(a + A)^2} & E &= \text{nuclear charge} \end{aligned} \right\} \quad . \quad . \quad (2)$$

The condition imposed by the quantum theory is that the moment of momentum p for the complete system, must equal a multiple of the quantity $\frac{h}{2\pi}$. The momenta concerned equal $mA\omega$ and $Ma\omega$ acting at perpendicular distances from the centre, equal to A and a respectively. Hence

$$p = mA(a + A)\omega = \frac{nh}{2\pi}.$$

To apply Bohr's postulate determining the emitted frequencies $\left(\nu = \frac{\Delta W}{h} \right)$, we must obtain the energy.

The mutual potential energy of the two charged masses equals $-\frac{eE}{a + A}$. The kinetic energy equals in amount exactly one half

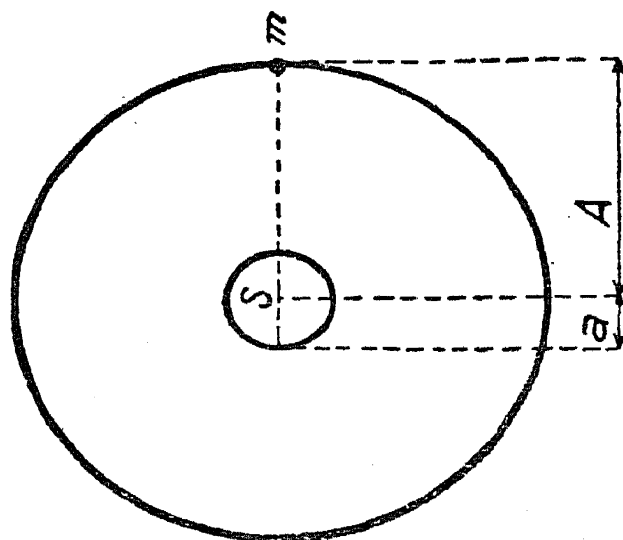


FIG. 5.

the potential energy, but is of opposite sign, just as in the case treated previously. This relation is, in fact, true generally for any system of material points between which forces are exerted which vary in inverse ratio to the square of the distance apart of the attracting bodies. The following holds always :

$$\text{Mean kinetic energy} = -\frac{1}{2} \text{ mean potential energy} = -\text{total energy}.$$

It should be observed that, in the above, *mean* kinetic and *mean* potential energy are referred to, for in general these vary during the motion. For example, in the motion of a planet round the sun in an elliptical orbit, the velocity and potential energy vary from instant to instant as the length of the radius vector alters.

To return to the immediate problem, calculation of the total energy of the system in the orbit characterised by the quantum number n , yields the important result,

$$\text{Total energy} = -\frac{2\pi^2 e^2 E^2}{n^2 h^2} \frac{Mm}{M+m}.*$$

The general expression for the emitted frequencies is obtained immediately from the energy formula by applying Bohr's postulate

$$\nu = \frac{\Delta W}{h}.$$

It is seen that the result obtained is the same as that previously arrived at by neglecting the motion of the nucleus, except in one particular, the replacement of the electronic mass m by the

expression $\frac{Mm}{M+m}$ which coincides with m only if the nuclear mass is infinitely great compared with the electronic mass. Actually for hydrogen $\frac{M}{m}$ equal 1,840, and for ionised helium, 7,360.

The factor ν_0 no longer equals $\frac{2\pi^2 m e^4}{h^3}$, but becomes instead

$$\frac{2\pi^2 m e^4}{h^3 \left(1 + \frac{m}{M}\right)} = \frac{R_\infty}{1 + \frac{m}{M}}$$

$$* \text{ E}_{\text{pot}} = -\frac{Ee}{a+A} = -\frac{4\pi^2 e^2 E^2}{n^2 h^2} \frac{Mm}{M+m}. \quad \text{E}_{\text{kin}} = -\frac{1}{2} \text{ E}_{\text{pot}}.$$

where R_∞ is the value assumed by R when the nucleus has infinite mass.

It is evident that the new R ought to depend on the ratio of the masses $\frac{m}{M}$, and not on their separate values, because the disposition of the rotating masses, that is, the relative values of the radii a and A , depends only on $\frac{m}{M}$ (see equation (1)) and not on the separate values of the masses.

Rydberg's constant R has its least value in the case of hydrogen. Putting, for hydrogen,

$$R_{\text{hydrogen}} = \frac{R_\infty}{1 + \frac{m}{M}}$$

we shall have for helium,

$$R_{\text{helium}} = \frac{R_\infty}{1 + \frac{1}{4} \frac{m}{M}}.*$$

There emerges from these two equations the possibility of determining the ratio $\frac{m}{M}$, from spectroscopic data. Eliminating R_∞ between the two equations, we obtain

$$\frac{m}{M} = \frac{R_{\text{hel}} - R_{\text{hyd}}}{R_{\text{hyd}} - \frac{1}{4} R_{\text{hel}}}.$$

The quantities R_{hel} and R_{hyd} are furnished by experimental spectroscopy.

Knowing the ratio $\frac{m}{M}$, we possess a means for determining accurately the ratio $\frac{e}{m}$ for the electron, *i.e.*, the specific charge of the electron. For $\frac{m}{M} = \frac{e}{M} / \frac{e}{m}$ and $\frac{e}{M}$ is merely the charge carried by one

* Since the mass of the helium nucleus is four times that of the hydrogen nucleus.

gramme ion of hydrogen, a constant known with great accuracy (96,494 Coulombs). Applying this method, $\frac{e}{m}$ comes out to be 5.31×10^{17} electrostatic units. This result is more accurate than that determined from the deflection of cathode rays in combined electric and magnetic fields. We may ask how it was possible, in practice, to determine the difference between the Rydberg constants R_{hyd} and R_{hel} appropriate to hydrogen and helium respectively. Consider a mixture of hydrogen and ionised helium emitting radiation. Confining our attention to the lines corresponding to the Balmer series of hydrogen defined by $\nu = \nu_0 \left(\frac{1}{2^2} - \frac{1}{n^2} \right)$, we have seen that for ionised helium there is a series, $\nu = 4\nu_0 \left(\frac{1}{4^2} - \frac{1}{k^2} \right)$, which when k is even, would give lines coinciding exactly with those of hydrogen, if the constants ν_0 occurring in the two formulæ were identical, *i.e.*, if the effect of nuclear motion were non-existent. Actually, the spectral lines of ionised helium observed on the same screen, or photographed together with those of hydrogen, are alternately remote from and very close to Balmer lines.

Paschen, who carried out special experiments on this point, found :

	Wave-length in Ångström Units	
	Ionised Helium	Hydrogen
$k = 8$	4,859.3	4,861.3 H β
$= 9$	4,561.6	—
$= 10$	4,338.7	4,340.5 H γ
$= 11$	4,199.9	—
$= 12$	4,100.0	4,101.7 H δ

From the differences in wave-length of corresponding lines of ionised helium and hydrogen, Paschen determined the two

constants R with great accuracy. He found for hydrogen $R = 109677 \times 3.10^{10}$, for helium $R = 109722 \times 3.10^{10}$.

The Elliptical Orbits of the Hydrogen Atom

Bohr's theory has other successes to its credit, but before discussing the advance made by Sommerfeld in about the year 1918, it may be well to point out that this method of approach to the problem of the emission of spectral lines is to-day mainly of historical importance. The successful conceptions of Bohr and Sommerfeld have been merged into a more general theory which in the last few years has assumed a definite form under the name of "quantum mechanics."

Up to now we have discussed the spectral lines of hydrogen and ionised helium as if only circular orbits need be considered. Actually, however, observations with spectrographs of high resolving power show that the individual lines are formed of several closely adjacent components which are distinguishable as separate lines only if spectrographs are available, capable of producing sensible displacements despite the small differences of frequency involved. This complexity suggested the idea that the possible orbits were more numerous than was admitted in Bohr's original theory, and Sommerfeld was led to ask himself whether, besides all the circular orbits, the electron of the hydrogen atom might not also describe ellipses. This notion seems natural enough when it is recalled that one heavenly body gravitating about another moves in just such an elliptical orbit, which may be more or less elongated, the circle being merely a particular case in the infinity of ellipses. The multiplicity of elliptical orbits is twofold, there are larger and smaller ellipses, ellipses of greater or less eccentricity.

If the hypothesis in question is true, the elliptical orbits should present the same discontinuous character as the circular ones. This follows from the observed sharpness of spectral lines comprising several separate components, the origin of which it is sought to explain. Thus, following up Sommerfeld's suggestion, a principle was sought for by means of which, from among the infinity of ellipses provided by classical mechanics as possible

orbits, those actually capable of existing in the atom, were singled out. The frequency corresponding to the passage of an electron from one of these orbits to another would then be defined by the

usual relation $\nu = \frac{\Delta W}{h}$.

It was of course necessary that the rule for the selection of the elliptical orbits should agree with the procedure adopted by Bohr in the case of circular orbits, the circle being merely a special case of the ellipse.

To avoid interrupting the discussion of fundamental principles, with detailed calculations, we shall limit ourselves at this point to giving a general idea of the solution to the problem in question.

The motion of the electron is one of two degrees of freedom, two parameters defining an ellipse, the two axes or one axis and the eccentricity.

As previously noted, Bohr's condition for selecting the circular stationary orbits from among the infinitely many allowed by classical mechanics, was :

$$\text{momentum} \times \text{length of orbit} = \text{a multiple of the quantum of action } h,$$

or, in symbols,

$$mvr \Sigma d\phi = 2\pi mvr = nh$$

where $\Sigma d\phi$ represents the sum of the angular elements $d\phi$ described in one revolution.

The closely analogous conditions chosen by Sommerfeld, were :

$$\int p_{\phi} d\phi = n_1 h$$

$$\int p_r dr = n_2 h,$$

p_{ϕ} being the moment of momentum, p_r the radial component of the momentum. The first relation states that the integral or sum of the elements $p_{\phi} d\phi$ extended over a complete revolution equals an integral multiple of the constant h . The second relation states that the integral of the elements $p_r dr$ extended over a complete revolution, also equals an integral multiple of h .

A few words of explanation with regard to the quantities p_ϕ and p_r may be useful. The mass point (in our case the electron) describing its elliptical path will, at a given instant, have the velocity v , v being a vector resolvable into the radial component of velocity, v_r , and the azimuthal component v_ϕ (see Fig. 6). The radial component of the momentum p_r will equal mv_r , and the moment of the momentum p_ϕ will clearly be given by the product, azimuthal momentum mv_ϕ times the radius vector r , *i.e.* by

$mv_\phi r$. Putting $v_\phi = r \frac{d\phi}{dt}$

the moment of momentum becomes $mr^2 \frac{d\phi}{dt}$. Now this

expression remains the same at whatever point of the elliptical orbit the mass point may be, for a famous law of Kepler's states that the area swept over in unit time by the radius vector

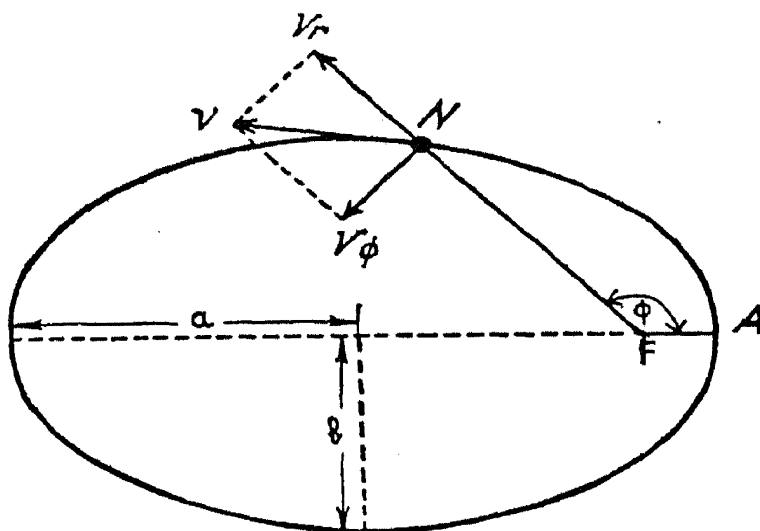


FIG. 6.

drawn from the planet to the sun is constant during the motion, and this area is in fact given by $\frac{1}{2} r^2 \frac{d\phi}{dt}$.

To sum up, Sommerfeld's conditions for selecting the stationary elliptical orbits in which the hydrogen electron might move, were :

$$\int_0^{2\pi} p_\phi d\phi = 2\pi p_\phi = n_1 h \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\int_{\phi=0}^{\phi=2\pi} p_r dr = n_2 h \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

By choosing arbitrarily any two whole numbers n_1 and n_2 , the elliptical orbit is determined and, at the same time, the energy of the electron moving in the orbit, is fixed. Knowing the energies corresponding to the different orbits, the frequency emitted in the act of transition from one orbit to the other follows from the

usual law $\nu = \frac{\Delta W}{h}$, and formulæ for the spectral series are obtained.

It will not have escaped notice that Sommerfeld's *quantum conditions* are in complete agreement with Bohr's single condition.

The important result obtained from Sommerfeld's calculations for the energy corresponding to a stationary orbit runs as follows :
energy corresponding to an orbit defined by the two quantum numbers $n_1 n_2$,

$$W = \frac{2\pi^2 m e^2 E^2}{h^2} \frac{1}{(n_1 + n_2)^2} \cdot \cdot \cdot \cdot \cdot \cdot (3)$$

The calculations also showed that the semi axes of the ellipse determined by the two arbitrarily chosen quantum numbers $n_1 n_2$ had the values :

$$\text{semi major axis } a = \frac{h^2}{4\pi^2 m e E} (n_1 + n_2)^2 \cdot \cdot \cdot (4)$$

$$\text{semi minor axis } b = a \frac{n_1}{n_1 + n_2} \cdot \cdot \cdot \cdot \cdot (5)$$

From these expressions an important consequence is deduced. The energy W is the sole quantity determining the monochromatic

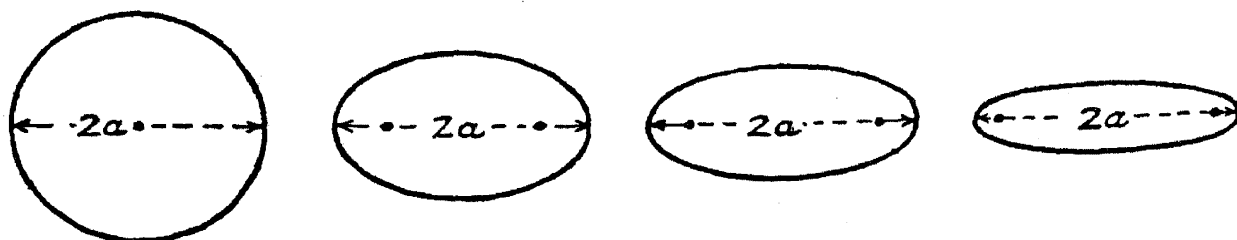


FIG. 7.

frequency emitted by the atom when the electron passes from one energy level to another. Equation (3) indicates however that many pairs of quantum numbers $n_1 n_2$, lead to ellipses of the same energy, in fact all pairs $n_1 n_2$ such that the sum $n_1 + n_2$ is constant.

For example, if $n_1 + n_2 = 4$, n_1 may have any of the values 1, 2, 3 or 4, n_2 having the corresponding value 3, 2, 1 or 0. The ellipses corresponding to these pairs of quantum numbers will, by

virtue of formula (4), all have the same major axis. On the other hand, their eccentricities will differ (see Fig. 7).

The nucleus, where the charge E is concentrated (for hydrogen E equals e), occupies one of the foci of the ellipse, and in the case of a circle is at the centre; n_2 is then zero and $b = a$, by formula (5).

To return to the most important aspect of the theory, the expression for the emitted frequency is given by Bohr's postulate

$\nu = \frac{\Delta W}{h}$. For the elliptical orbits of the hydrogen atom (and generally for a nuclear charge E about which rotates an electron of charge e) the frequency is defined by the expression,

$$\text{frequency } \nu = \frac{2\pi^2 m e^2 E^2}{h^3} \left[\frac{1}{(n_1 + n_2)^2} - \frac{1}{(m_1 + m_2)^2} \right]. \quad (6)$$

The pair of numbers $m_1 m_2$, refer to the initial orbit, $n_1 n_2$ to the final orbit.

Comparing the above expression with that giving the frequency for circular orbits,

$$\nu = \frac{2\pi^2 m e^2 E^2}{h^3} \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

it is immediately obvious that *the theory of elliptical orbits predicts precisely the same series of lines*. For example, if $n_1 = 1$, $n_2 = 2$, $n = n_1 + n_2$ will equal 3 and the energy will assume the same value as in a circular orbit with quantum number $n = 3$.

Thus as regards the multiplicity of spectral lines, the hypothesis of elliptical orbits yields nothing more than Bohr's theory. The only difference consists in the fact that this hypothesis of Sommerfeld's admits the emission of a given line in more than one way. This point will be better understood in the sequel.

No explanation is obtained in this way, of the complexity of the spectrum, the fact that one line is seen split into several components when a spectrometer of high resolving power* is employed. Nor has the motion of the nucleus anything to do

* That is, capable of separating two monochromatic radiations of nearly the same frequency.

with the splitting up of the lines for, as in the case of circular orbits, the effect results merely in the substitution of the mass

$$\frac{m}{1 + \frac{m}{M}}$$

for the true mass of the electron, m , in the frequency formula.

This modification introduces a *general shift* of all the lines without however increasing their number.

Effect of the Variation of Electronic Mass with Velocity

In the above calculations one aspect of the problem has been passed over. It has in fact been supposed that the mass of the electron is constant. The theory of relativity indicates however that the mass of the electron depends on its velocity, and in our case the electron velocity varies from point to point in the elliptical orbit, just as the earth in its path moves more quickly when it is near to the sun than when it is at a greater distance away.

It was stated above that to the pairs of quantum numbers $n_1 n_2$ giving a specified value for the sum $(n_1 + n_2)$, there corresponded elliptical orbits of different eccentricities, but all representing the same total energy of the electron. It was also shown that these orbits all yielded the same frequency when the electron passed from one of them, to the same final orbit. When allowance is made for the variability of mass of the electron however, these elliptical orbits are transformed into unclosed trajectories (see Fig. 8), and the electron no longer has the same energy in all. These open orbits bring to light numerous lines which formerly were superposed one on another; there occurs in fact a subdivision of single lines into components.

The problem was attacked mathematically by Sommerfeld, in 1915, who showed that an electron, whose mass varies continuously from point to point in its orbit according to the relativistic law

$$m = \frac{m_0}{\sqrt{1 - \frac{v^2}{c^2}}}$$

describes not an ellipse, but a complicated curve

which can be constructed graphically by imagining a point to

move in an elliptical path on a surface whilst the surface itself rotates slowly and continuously about the focus (see Fig. 8).

The general expression for the total energy corresponding to an orbit is still defined by two quantum numbers, but takes the following form :

total energy of the electron

$$W = \frac{2\pi^2 n m e^2 E^2}{h^2} \left[\frac{1}{(n_1 + n_2)^2} + \frac{\alpha^2 Z^2}{(n_1 + n_2)^4} \left(\frac{1}{4} + \frac{n_2}{n_1} \right) + \dots \right] \quad (7)$$

This expression is only approximate as it is limited to the first terms of an expansion in series, but that is unimportant. E , it will be remembered, is the charge on the nucleus, which is situated at the focus. The symbol α stands for the expression $\frac{2\pi e^2}{hc}$, c being the velocity of light.* It is immediately clear from equation (7) that, keeping $n_1 + n_2$ constant, different energies are obtained for the orbits corresponding to different selections of the pair of quantum numbers n_1 n_2 . This follows because in (7),

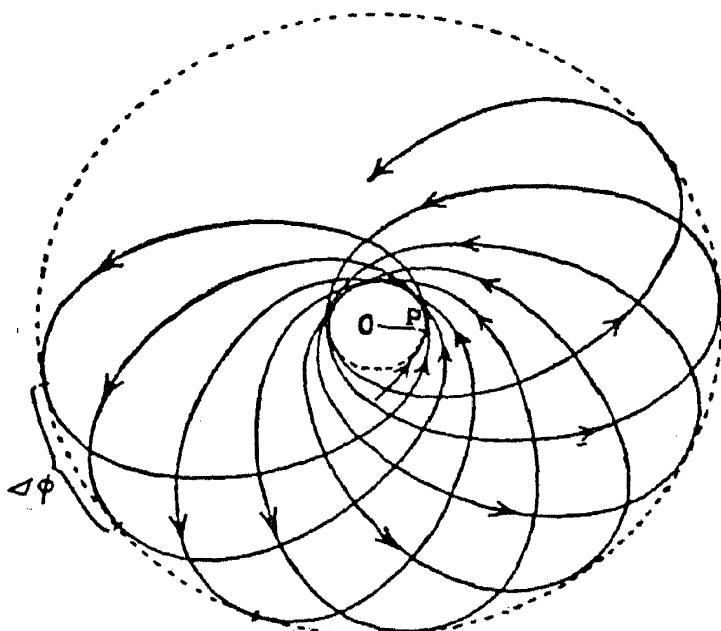


FIG. 8.

besides the sum $n_1 + n_2$, the ratio $\frac{n_2}{n_1}$ also appears. Thus, for example, the solutions $(n_1 = 1, n_2 = 6)$, $(n_1 = 2, n_2 = 5)$, $(n_1 = 3, n_2 = 4)$, etc., are not equivalent in respect of the orbital energy, and hence, of the emitted frequency resulting therefrom by an application of Bohr's postulate $\nu = \frac{\Delta W}{h}$.

This is a very important result. The details of the calculations

* α is termed the fine structure constant :

$$\alpha = \frac{2\pi e^2}{hc} = 7.283 \times 10^{-3} \text{ and } \alpha^2 = 5.305 \times 10^{-5}.$$

which will be gone into a little more fully in the next chapter, are omitted here, and we confine ourselves to giving a general outline of the reasoning.

The fact of the existence of closely-spaced groups of lines which arise, so to speak, from a line which ought to be single, constitutes what is called the *fine structure of spectral lines*. The name is very appropriate, for actually the correction term distinguishing (7) from (3) (which neglects relativity), is extraordinarily small, involving, as it does, the factor $\alpha^2 = 5.305 \times 10^{-5}$.

To take a concrete example, consider the Balmer series which arises, as we know, by the passage of the electron from various outer orbits, to the second orbit, the so-called two quantum orbit for which $n_1 + n_2 = 2$. To obtain the fine structure of the Balmer series, we must first study the case of a circular orbit ($n_2 = 0$), and consider transitions to this orbit. The calculations must then be repeated for transitions to the elliptical orbit whose quantum numbers are $n_1 = 1, n_2 = 1$.

The desired information is contained in (7). For the circle ($n_1 = 2, n_2 = 0$) the correction term $\frac{\alpha^2 Z^2}{(n_1 + n_2)^4} \left(\frac{1}{4} + \frac{n_2}{n_1} \right)$ takes the value $\frac{\alpha^2 \cdot 1}{2^4} \left(\frac{1}{4} + 0 \right) = \frac{5.305 \times 10^{-5}}{2^4} \cdot \frac{1}{4}$.

For the ellipse ($n_1 = 1, n_2 = 1$) the correction term becomes

$$\frac{\alpha^2 \cdot 1}{2^4} \left(\frac{1}{4} + 1 \right) = \frac{5.305 \times 10^{-5}}{2^4} \left(1 + \frac{1}{4} \right).$$

Thus the *difference* between these two correction terms, which determines the difference of the frequencies for the two cases,

obtained by applying the formula $\nu = \frac{\Delta W}{h}$, amounts to $\frac{5.305 \times 10^{-5}}{16} = 3 \times 10^{-6}$, and the general conclusion arrived at

for this particular case is that every line is replaced by a *doublet* the components of which are separated by 0.16 of an Ångström unit

Although for $n_1 + n_2 = 2$ there are only two possible cases, it

is clear that the number will increase very rapidly for other values of the sum $n_1 + n_2$, and these possible cases will combine with possible cases for the sum $m_1 + m_2$, giving rise to a great multiplicity of lines in the spectrum. It is with this complex of lines that we are concerned in the study of fine structure.

Without entering further into details, we pass to the following general observations.

The reader will have noticed that the case in which the azimuthal quantum number n has the value zero has never been admitted as a possible state. This is because, for $n_1 = 0$, the corresponding ellipse would be drawn out into a straight line passing through the nucleus, and it is evidently impossible for the electron (which is a negative charge), instead of gravitating round the nuclear charge, to fall into the nucleus and then pass beyond, in an oscillatory motion.

The other observation is that not all the theoretically possible transitions of the electron from one elliptical orbit to another, mentioned above, actually occur. In other words, taking four arbitrarily chosen integers $n_1 n_2 m_1 m_2$, it does not follow that an electron transition from the orbit $n_1 n_2$ to the orbit $m_1 m_2$ will be permissible. According to the so-called *selection principle*, transitions are only possible between orbits for which the azimuthal quantum numbers, $n_1 m_1$ respectively, differ by

$$\text{zero, } +1 \text{ or } -1.$$

This principle limits in some degree the number of possible lines, for, among all imaginable combinations, only those in which the azimuthal quantum numbers differ by unity, are observed.

The selection principle will be further discussed in Chap. VI.

Evaluation of the Universal Constants h , e , m from Spectroscopic Data

The frequencies of the series of lines emitted by hydrogen are expressible in terms of Planck's constant h , the electronic charge e and the electronic mass m . It is possible, starting from spectroscopic measurements to work back and determine the numerical values of these important constants. The calculation

is the more interesting because in the last ten years wave-length determinations have reached a very high precision, and the values of the three constants can be fixed with great exactness.

On p. 49 it was explained how the constants ν_0 , corresponding to hydrogen and ionised helium, yield a numerical result for the ratio $\frac{e}{m}$, the specific charge of the electron. This represents the first step in the calculation. The ratio e/m was found to equal 5.31×10^{17} electrostatic units.

From an examination of the hydrogen spectrum which exhibits fine structure, it is possible to obtain the value of the factor α^2 on which the magnitude of the *fine structure* depends. We know in fact that

$$\alpha^2 = \left(\frac{2\pi e^2}{hc} \right)^2 = 5.305 \times 10^{-5} \quad . \quad . \quad . \quad (1)$$

This result determines the numerical value of $\frac{e^2}{h}$.

Finally, the value of the coefficient ν_0 , occurring in Bohr's general expression, is known to equal $109,737.11 \times 3 \times 10^{10}$.

Hence, since

$$\nu_0 = 2\pi m \frac{e^4}{h^3} = 2\pi \left(\frac{e^2}{h} \right)^3 / \left(e \cdot \frac{e}{m} \right) \quad . \quad . \quad . \quad (2)$$

by inserting the known numerical values of ν_0 , $\frac{e^2}{h}$, and $\frac{e}{m}$, a simple equation for e is obtained leading to the result $e = 4.77 \times 10^{-10}$. Equation (1) then gives for Planck's constant, $h = 6.55 \times 10^{-27}$. Knowing e and $\frac{e}{m}$, the value of m is obtained at once.

To sum up, *starting from spectroscopic observations only*, modern physics derives the following results :

$e = 4.77 \times 10^{-10}$ electrostatic units	$m = 0.9 \times 10^{-27}$ gm.	$h = 6.55 \times 10^{-27}$ erg × sec.
<i>charge of the</i> <i>electron</i>	<i>mass of the</i> <i>electron</i>	<i>Planck's constant.</i>

These values agree perfectly with Millikan's direct determination

of e , and the results for e and m furnished by cathode ray deflection experiments. As regards Planck's constant h , the value obtained from a study of the energy distribution in the black body spectrum is 6.55×10^{-27} . There are however many other methods for determining h and some of these will be touched upon later.

Other Problems Connected with the Hydrogen Atom

Having dealt with the problem of the elliptic orbits of the hydrogen atom, the effect of the nuclear mass, and the fine structure resulting from the variation of the electron mass with velocity, it remains to consider two other questions pertaining to the hydrogen atom, namely, the motion of the electron (α) in an electric, (β) in a magnetic field.

It is obvious that the motion becomes very complicated, and the result is an increase in the number of spectral lines emitted. These problems were attacked by the leading mathematical physicists—Lorentz, Sommerfeld, Epstein, Schwarzschild, Debye, Larmor, etc.—and complete solutions have been obtained. These call for some knowledge of the analysis involved, and it has been considered desirable to relegate them to a separate chapter, where these more difficult matters will be collected together.

In the following chapter the opportunity is also taken to explain in detail the method by which Sommerfeld succeeded in obtaining the fine structure of the spectral lines of hydrogen.

The Different Energy Levels of the Hydrogen Atom

The hydrogen atom, in its normal state, consists of a nucleus about which a single electron rotates in a circular orbit of radius 0.53×10^{-8} cms. Despite the extreme simplicity of this structure, hydrogen, as we know, gives rise when suitably excited (collisions, electric discharge), to a complicated line spectrum extending from the ultra-violet to the infra-red and classifiable in the three famous series of Lyman, Balmer and Paschen. To explain this condition of affairs, Bohr supposes that the electron can be removed from the normal orbit and made to occupy other stationary energy states defined by the quantum conditions, these states or energy

levels corresponding to the various possible orbits. Whilst, however, the supposition of orbits is an interpretation in terms of a model, the existence of energy levels is an actual fact, as is shown by excitation phenomena, which will be described later, and by the corpuscular spectra, discussed in Chap. V. It is possible not only to establish the existence of these levels but also to measure their values. We shall meet with several experimental

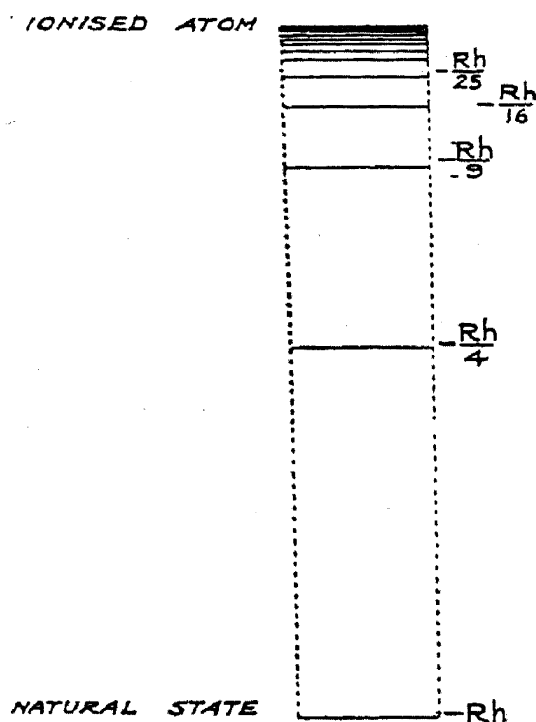


FIG. 9.

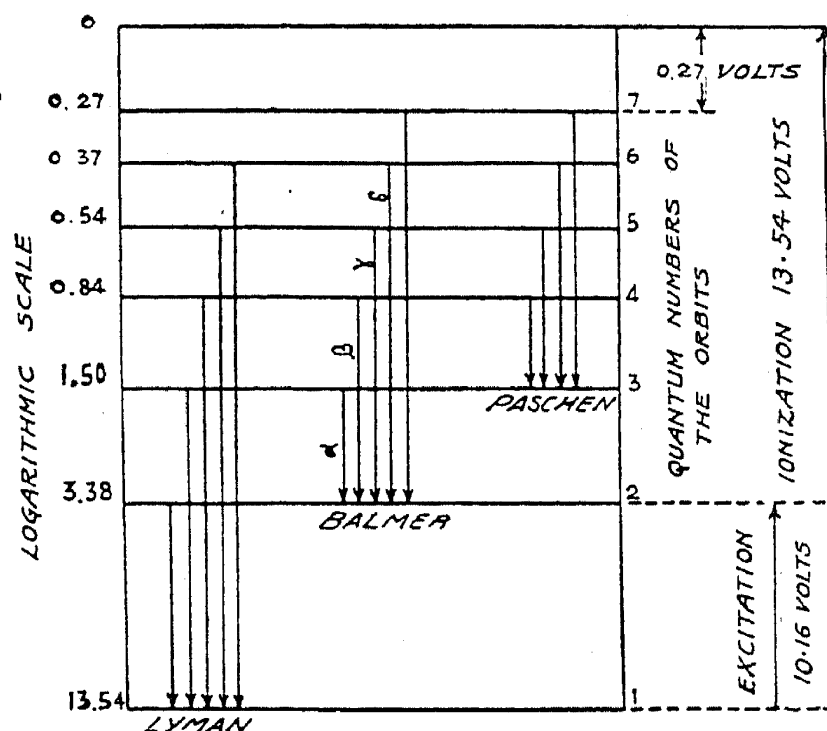


FIG. 10.—Energy Levels of Hydrogen, in Volts.

methods for demonstrating and assigning values to the energy levels.

Having emphasised this important point, we return to the hydrogen atom. We combine in one diagram the different energy levels computed for the successive circular orbits of quantum numbers 1, 2, 3, etc., for which the energies vary as the series, $1, \frac{1}{2^2}, \frac{1}{3^2}, \frac{1}{4^2}$, etc. The levels of the hydrogen atom obtained in this way are shown in Fig. 9.

The hydrogen spectrum, extending from the extreme ultra-violet to the infra-red can be classified, we repeat, in three simple series known by the names Lyman, Balmer and Paschen. The origin

of the lines in these series is shown clearly in the diagram of Fig. 10. The energy in the various levels which the electron can occupy is expressed in *volts*. For example, the energy necessary to transfer the electron from the normal state or first level, to an infinite distance, is equal to the energy acquired by an electron in falling freely between two points whose difference of potential equals 13.54 volts. As succeeding levels have energies which decrease in proportion to $\frac{1}{4}, \frac{1}{9}, \frac{1}{16} \dots$, all the levels are determined and consequently the frequencies of the various lines.

This diagram summarises the process of excitation which takes place in a discharge tube containing hydrogen gas subjected to electric bombardment. Certain molecules are dissociated into free atoms, and these, either by collisions or through some other cause, become "excited," that is to say, the electron is removed from its natural level to a level of higher energy. After a brief interval, the electron returns to a level of lower energy, with emission of the frequency characteristic of the transition process, which is given always by the formula $\nu = \frac{\Delta W}{h}$. At each instant, there will be atoms in all possible conditions of excitation.

From what has been said it is clear that the interpretation of spectra can be based exclusively on the consideration of energy levels without its being necessary to assume anything about the character of the orbits described by the electron. A further important consideration must be mentioned at this point. In studying the motion of the electrons of a more complicated atom or of a molecule, with the object of determining the orbits, it should be found that the energy of the system in one of its stationary states (for example, the normal state) agrees exactly with the actual energy appropriate to the state in question. If, in particular, this is the *normal* state, the theoretical energy should equal the energy necessary to ionise the atom, as given by experiment.

If the theoretical and experimental values do not agree, the *model* must be rejected. This is just what has happened in the case of the helium atom, and the hydrogen molecule, despite the

simplicity of the structures concerned. Only quantum mechanics gives the correct solution to these problems.

• Direct Evidence for the Existence of Stationary States for all Atoms. Spectral Terms

Consider a tube filled with helium gas and containing an incandescent filament from which electrons are emitted. By applying a potential difference between the filament and a fine metallic gauze placed in front of it, the electrons are accelerated and pass through the gas with an energy which is accurately controlled by the applied potential difference. A third electrode is maintained at a potential slightly higher than that of the filament, so that to reach this electrode the electrons proceeding from the metallic grid must sacrifice nearly all the energy they have acquired. If the electrons lose no energy in traversing the gas, they just reach the third electrode, in the same way as water, having acquired energy in falling, rises again to the level of the source. If, however, the electrons lose energy by transferring it to the atoms with which they collide, it is then impossible for them to reach the third electrode.

By measuring the current to the third electrode it is found that if the electrons have energy less than that acquired in falling through 19.75 volts, practically no energy is lost in passing through the gas. If the electrons have energy exceeding the equivalent of 19.75 volts, they can give up some portion of it and, in fact are able to consign the equivalent of 19.75 volts to the gas, the balance being retained by the electrons. One concludes from this that the helium atom with which an electron has collided, can annexe exactly 19.75 units of energy (in the volt scale), neither more nor less.

Similar experiments show, for example, that the mercury atom can receive from an electron the energy 4.66 volts, no more and no less, the sodium atom appropriates to itself 2.1 volts, and so on.

Another way of expressing the same fact is the following. The helium atom can exist, in general transiently, not only in its normal state, but also in a second, so-called, excited state. It cannot however exist in intermediate energy states. There may

be several successive excited states or energy levels, but these are always discrete. Examples are given in the following Table :

	Helium.	Neon.	Sodium.	Magnesium.	Mercury.
Energy * in the normal state	0	0	0	0	0
First excited state	19.75	16.65	2.1	2.7	4.66
Second excited state	20.55	18.45		4.4	$\begin{cases} 4.86 \\ 5.43 \\ 6.7 \end{cases}$
Ionised atom	24.5	21.5	5.12	7.6	10.4

In the above Table are also indicated the amounts of energy required to ionise the atom, that is, to expel an electron. Generally the energy levels are expressed by giving the difference of energy between the given level and the ionised atom. Thus for mercury the following numbers are obtained for the various energy levels :

energy in the ionised state : — 0.
possible energy states : — 3.7, — 4.97, — 5.54,
— 5.74 volts.

normal state (also state of least energy) : — 10.4 volts.

In particular, for hydrogen we have seen that the levels possess the energies $-\frac{Rh}{1} - \frac{Rh}{4} - \frac{Rh}{9} \dots$

This question has been treated very briefly here, but it will be returned to shortly when a fuller description of the various methods leading to the determination of energy levels will be given.

With every atom are associated its *spectral terms*, a series of values T defined in such a way that their differences yield the frequencies divided by the velocity of light. We recall in this connection that Bohr's postulate $W_1 - W_2 = h\nu$ supplies the connection between frequencies and energy levels. In practice

* These values of the energy are given in volts because the potentials necessary to cause the electron to change its level, multiplied by the electronic charge e , give precisely the values of the energy difference between the initial and final levels.

we speak commonly of spectral terms which are defined by the relation $T_1 - T_2 = \frac{1}{ch} (W_1 - W_2) = \frac{\nu}{c}$ wave-lengths per centimetre. Thus the difference between two terms equals the reciprocal of the wave-length. The term $\frac{\nu}{c}$ of greatest numerical value is called the fundamental term of the atom. For sodium this has the value 41,449.

*** Experiments of Barnes on the Capture of Electrons by α -Particles and the Energy Levels of the Helium Atom**

These interesting experiments were completed by Barnes and Davis in 1929.* A current of electrons is superposed on a beam of α -particles and the

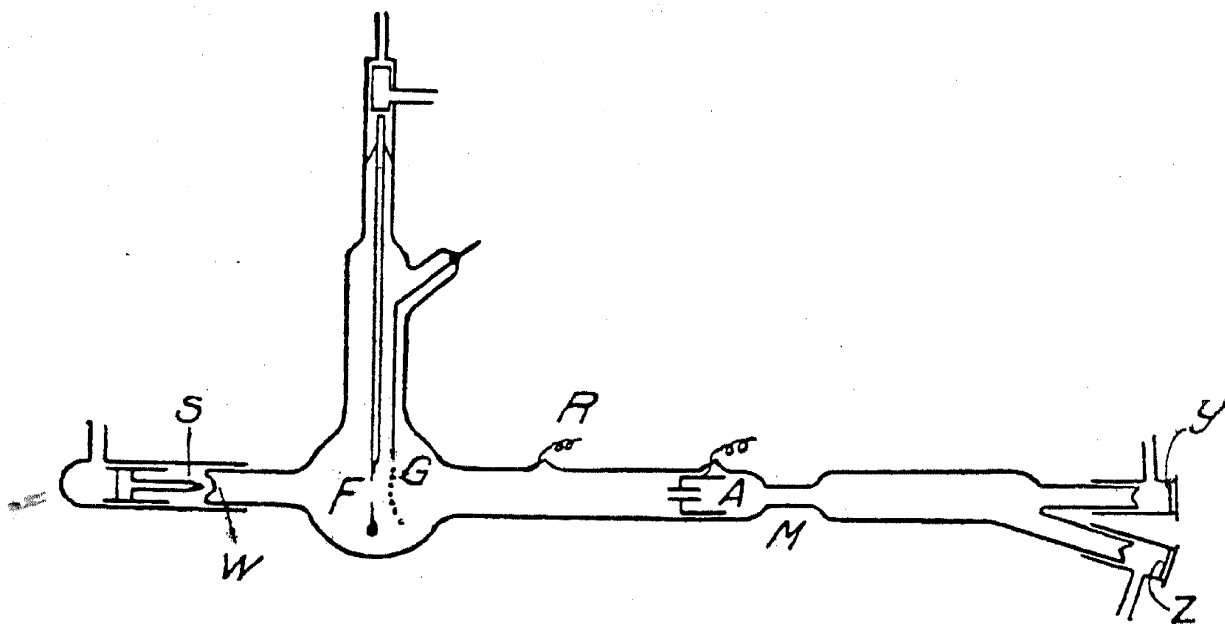


FIG. 11.

latter are subsequently deviated by a magnetic field. The α -particles are counted by observing scintillations on a suitable screen. Particles which have captured two electrons in their paths are not deviated and the decrease in the number of scintillations provides a measure of the frequency of such double captures. It is also possible to measure the number of captures of a single electron, using an apparatus similar although not identical with that shown in Fig. 11.

Barnes obtained the following important results. Electrons are captured when their velocity equals that of the α -particles or when their velocity relative to that of the α -particles has certain *discrete* values. In fact, combination of a single electron with an α -particle occurs when *the kinetic*

* Bergen, Davis and A. Barnes, *Phys. Rev.*, 34, p. 152, 1929. A. Barnes, *Phys. Rev.*, 35, p. 127, 1930.

energy of the motion of the electron relative to that of the α -particle, is equal to an energy level of the ionised atom. Similarly, in the case of double capture, the sum of the kinetic energies of the two electrons corresponds to an energy level of the helium atom (either parahelium or orthohelium).

Now, as the absorbing α -particle functions as nucleus of the atom which is formed, it follows from these experiments that for the capture to take place the kinetic energy of the electron in its motion relative to the nucleus, must be either zero or equal to the energy of a quantum state of the atom.*

Fig. 11 gives an idea of the way in which these experiments are performed. The whole apparatus is evacuated. S is the radioactive source (polonium); A is a small aperture through which the α -particles pass to emerge at Y, or at Z when deviated by a magnetic field applied at M. F is the filament emitting electrons; G is a grid and the second anode is applied at A. The detecting screens are of zinc sulphide. To prevent any accumulation of charge on the glass walls, the latter are silvered.

The accelerating field acts between the filament and the grid, which are made concave in order to converge the electrons at A where the capture occurs. When the accelerating field is applied, there is a decrease in the number of scintillations at Z, because the diminished charge reduces the deflection, and from this the number of captures can be calculated.

The first result, as stated, is that this effect occurs for an accelerating field such that the velocity of the electrons is 1.44×10^8 cm./sec., which is precisely the velocity of the α -particles emitted by polonium.

The further observation is as follows. If v and u are respectively the velocities of an electron and an α -particle, then the kinetic energy of the electron with respect to the α -particle is $W = \frac{1}{2} m(v - u)^2$, where m is the mass of the electron. Let V_n and V_0 be the potential differences corresponding to electron velocities v and u respectively.

$$\text{Then :} \quad v = \left(\frac{2e \cdot V_n}{m} \right)^{\frac{1}{2}}, \quad u = \left(\frac{2e \cdot V_0}{m} \right)^{\frac{1}{2}},$$

and hence,

$$\frac{W}{e} = (V_n^{\frac{1}{2}} - V_0^{\frac{1}{2}})^2 \text{ in volts.}$$

Thus, substituting in this formula, for V_0 the potential necessary to make the electron velocity equal to that of the α -particles, and for V_n the successive potentials at which the phenomenon of capture is observed, a series of values of W is obtained, some corresponding to V_n greater and some to V_n less than V_0 .

Barnes obtained, for example :

Values of W/e for Simple Capture

$V_n < V_0$		$V_n > V_0$		Mean W/e .
V_n	W/e	V_n	W/e	
293	51.8	1005	54.9	53.2
418	14.8	800	15.6	15.2

The first and third columns contain the values of the potential at which capture occurs. In the experiments V_0 was 590 volts.

Values of W/e for Double Capture

$V_n < V_0.$		$2W/e.$	$V_n > V_0.$		$2W/e.$	Mean $2W/e.$
V_n	W/e		V_n	W/e		
327	38.6	77.2	930	38.6	76.8	77.0
338	38.4	70.8	931	36.0	72.0	71.4
347	32.1	64.2	907	33.6	67.2	65.7
603	28.4	56.8	885	29.7	59.4	58.1

It is seen that the values of W/e , obtained from the above formula expressing the energy as a function of the potential, are given, and then these are doubled because there are two electrons. The existence of discrete energy values is clearly indicated. In particular, the potential of 77 volts corresponds to the sum $24.5 + 54.16$, of which the first term is the ionisation potential of the neutral helium atom,* whilst the second term agrees with the potential obtained in the simple capture experiments and should equal four times the value 13.54, which is the ionisation potential of hydrogen. This is in fact the case.

The impressive result of these experiments is that the capture of the electron is governed by a definite energy condition, and, to be exact, that the phenomenon occurs when the kinetic energy of the electron with respect to the nucleus of the neutral atom formed in the process, is equal to a quantum level of the helium atom.

Distribution of Electrons in Different Levels

The considerations brought forward above and others which cannot be dealt with in detail, led Bohr to the idea that the peripheral electrons of an atom are distributed in various shells or levels. These shells (German : Schalen ; French : couches) were also called rings when, to begin with, Bohr supposed that the external electrons were arranged on plane concentric circular orbits. This conception had later to be rejected. The periodic variations in the properties of the elements brought out by Mendeleieff's classification had suggested the idea that the new electron which is added to the atom in passing from one element to the next, takes up its position in the outermost ring until the ring is completed. When this occurs a new ring appears. It seemed certain that the physical and chemical properties would depend directly on the peripheral electrons. Periodic variations in these properties would be obtained as a simple consequence of the formation, at regular intervals, of a new ring which, as it developed in the course of a period, would pass through the same

* See p. 93 for the method of Franck and Hertz.

Periodic System of the Elements

Shells.	K.	L.	M.	N.	O.	P.	Q.
Subshells.	1s	2s 2p	3s 3p 3d	4s 4p 4d 4f	5s 5p 5d 5f 5g	6s 6p 6d	7s 7p
Element.							
1 H	1						
2 He	2						
3 Li	2	1					
4 Be	2	2					
5 B	2	2 (1)					
10 Ne	2	2 6					
11 Na	2	2 6	1				
12 Mg	2	2 6	2				
13 Al	2	2 6	2 (1)				
18 A	2	2 6	2 6				
19 K	2	2 6	2 6	1			
20 Ca	2	2 6	2 6	2			
21 Sc	2	2 6	2 6 1	(2)			
22 Ti	2	2 6	2 6 2	(2)			
29 Cu	2	2 6	2 6 10	1			
30 Zn	2	2 6	2 6 10	2			
31 Ga	2	2 6	2 6 10	2 1			
36 Kr	2	2 6	2 6 10	2 6			
37 Rb	2	2 6	2 6 10	2 6	1		
38 Sr	2	2 6	2 6 10	2 6	2		
39 Y	2	2 6	2 6 10	2 6 1	(2)		
40 Zr	2	2 6	2 6 10	2 6 2	(2)		
47 Ag	2	2 6	2 6 10	2 6 10	1		
48 Cd	2	2 6	2 6 10	2 6 10	2		
49 In	2	2 6	2 6 10	2 6 10	2 1		
54 X	2	2 6	2 6 10	2 6 10	2 6		
55 Cs	2	2 6	2 6 10	2 6 10	2 6	1	
56 Ba	2	2 6	2 6 10	2 6 10	2 6	2	
57 La	2	2 6	2 6 10	2 6 10	2 6 1	(2)	
58 Ce	2	2 6	2 6 10	2 6 10 1	2 6 1	(2)	
59 Pr	2	2 6	2 6 10	2 6 10 2	2 6 1	(2)	
71 Lu	2	2 6	2 6 10	2 6 10 14	2 6 1	(2)	
72 Hf	2	2 6	2 6 10	2 6 10 14	2 6 2	(2)	
79 Au	2	2 6	2 6 10	2 6 10 14	2 6 10	1	
80 Hg	2	2 6	2 6 10	2 6 10 14	2 6 10	2	
81 Tl	2	2 6	2 6 10	2 6 10 14	2 6 10	2 1	
86 Rn	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	
87 —	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	1
88 Ra	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6	2
89 Ac	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 1	(2)
90 Th	2	2 6	2 6 10	2 6 10 14	2 6 10	2 6 2	(2)

characteristic phases, determined by the number and the distribution of its component electrons.

Since the alkali metals are distinguished by the facility with which they lose an electron—when in contact with water or by the action of ultra-violet light—it was natural to think that the electron so weakly held was the sole occupant of the external ring.

The alkali earth metals (calcium magnesium, etc.) lose, less easily, two electrons, and both these would presumably be in the outermost ring. In this way the number of external electrons would gradually increase until the halogens (chlorine, bromine, etc.) were reached, after which the ring would be completed with the noble gases which follow ordinarily the respective halogens. It was considered that the completed ring of 8 electrons determined the chemical inactivity of the atom.

After the completion of a ring a new electron takes up its position in a new one, and so on. Since the atoms have about the same diameter, this mode of formation implies at once that the deepest levels during this building up process must approach closer to the nucleus, and the energy of the electron in these levels must increase.

The various groups were designated the K, L, M, N, O, P and Q shells, the K shell being closest to the nucleus.

The simple law of succession, with a periodicity of eight members, just given, holds actually only for the first part of the periodic system.

The various considerations which led Bohr, in 1922, to a complete formulation of the electron distribution in the different shells, each characterised by a given value of the total quantum number, cannot be entered into here. These considerations were based, in the first place, on the spectra of the elements, not only in the visible and ultra-violet but also in the X-ray region. In addition, use was made of ionisation potentials, radioactive properties, and, on the theoretical side, the correspondence principle. Bohr's ideas were developed independently by Stoner in 1924.*

In the above Table, we merely reproduce the results of these

* N. Bohr, "Der Bau der Atome u. die physikalischen u. chemischen Eigenschaften d. Elemente," *Zeits. f. Phys.*, 9, 1922. Stoner, "The Distribution of Electrons among Atomic Levels," *Phil. Mag.*, 48, 1928. Also, Main Smith, *Journ. Soc. Chem. Inst.*, 44, p. 944, 1925.

investigations, without going into details. For each element the Table gives the number of electrons in each shell and in each subshell. When we have discussed (in Chap. III) Pauli's principle, the internal quantum number and the rotating electron, we shall return to this subject and it will then be seen how this construction of the periodic system arises naturally, and the significance of the symbols $2s$, $2p$, $3s$, $3p$, etc., appearing at the top of the Table will become clear.

We limit ourselves at the moment to the remark that where numbers occur enclosed in brackets, attention is drawn to the fact that one or two electrons which are added to form successive elements, take their places in a shell (for example, the O shell), before the preceding shell (the N shell) has taken up its full complement of electrons. The determination of the maximum number of electrons in each shell is explained on p. 139.

It may be asked how it can ever come about that in the successive formation of the elements an electron places itself in, or continues to occupy, a shell when an interior shell is incomplete. This problem was attacked and solved by Fermi by means of his statistical method, in which the electrons surrounding the nucleus are treated as forming a kind of gaseous atmosphere to which statistical considerations are applicable.*

At the time when Bohr developed the theory of the periodic system, the element 72 had not been recognised, and it was thought that it would be a *rare earth*. According to Bohr's views, however, the number of rare earths could not exceed 15, and, hence, element 72 ought instead to resemble zirconium. As homologous elements frequently occur together in nature, the unknown element was to be sought for in zirconium minerals. It was therefore a striking achievement of Bohr's theory when, in 1922, Hevesy and Coster found that the new element was actually present in zirconium minerals. In honour of the city of Copenhagen, where the discovery was made, they called the new element *hafnium*, the Latin name of the city.

* For this theory see the paper by Professor Fermi, "Atti della R. Accademia dei Lincei," IV, 1928.

Examination of Stoner's Table shows that for chemically homologous elements the electrons of the external shell are in the same states. Examples of this principle are provided by the alkali metals, sodium, potassium, rubidium and caesium, and the elements copper, silver and gold. The metals boron, aluminium, gallium, indium and thallium all have an external shell containing three electrons for two of which $k = 1$, with $k = 2$ for the third electron. The noble gases all have completed external shells. These considerations bring out clearly the fact that the chemical properties of an element depend on the external electron shell. Thus, the metals of the rare earths have closely similar chemical properties because passing from the lightest (atomic number 58) to the heaviest (atomic number 71), 14 *internal* orbits of total quantum number 4, azimuthal quantum number 3, are filled up, the composition of the external shell remaining unchanged.

The Structure of the Atoms and X-ray Spectra *

The high frequency spectra of the elements are characterised by great simplicity. The regular way in which they vary as the atomic number of the element goes up indicates that they originate in the central regions of the atom, which are not subject to periodic changes. It is clear that this regularity, discovered by Moseley, should find its interpretation in Bohr's theory, and this will now be shown to be the case.

The X-rays of the K series are emitted by an electron which falls from a higher level to the innermost level, whilst the L and M series are generated when the fall is arrested at the second and third levels respectively. It is for this reason that the successive zones of electrons, starting from the centre, are denoted by the letters K, L, M, N, etc. (see Fig. 12).

For such an electron transition towards the interior to be possible; an electron must at some time have been elevated from one of the central shells. Experiment has shown that the various methods of excitation never produce, in these regions of the atom, a simple displacement of an electron from one orbit to another

* See Coster, "On the Spectra of X-rays and the Theory of Atomic Structure," *Phil. Mag.*, 44, p. 546, 1922.

more exterior, but effect the complete expulsion of the electron from the atom.

Under the action of light, the peripheral electrons are capable of being transferred to any of the higher orbits giving an absorption spectrum of lines similar to the emission spectrum (inversion of the Fraunhofer lines). This phenomenon is possible because the orbits are unoccupied in the normal state of the atom. For the central electrons, conditions are quite different in this respect, because the zones above are complete. Thus, excitation by cathode rays or primary X-rays will be without effect on any of these electrons, unless the electron is transferred to the exterior of the atom and expelled. This explains why the absorption spectra of X-rays are quite different in character from the emission spectra.

The cathode particles used to produce excitation are thus without effect so long as their energy remains below a certain limit. As the velocity of the cathode particles is increased, the rays of the M, L, K series are emitted in succession, all the rays of one series appear-

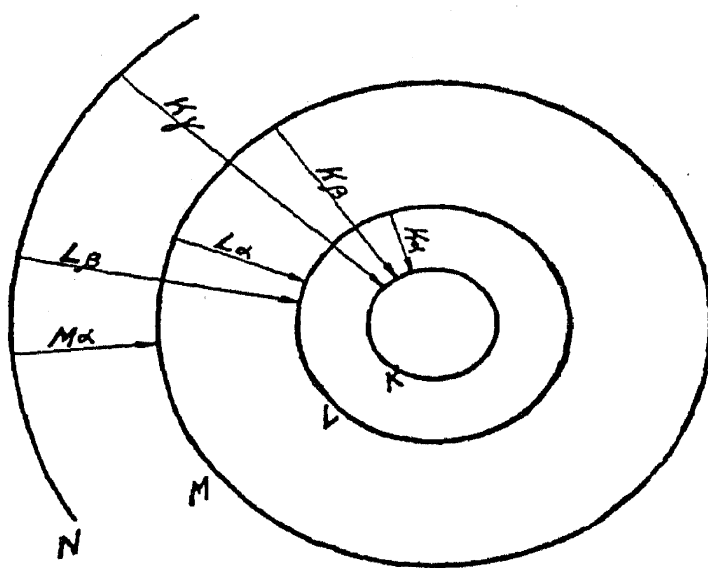


FIG. 12.

ing together. Each series begins to be radiated precisely at the instant when the energy of the cathode rays attains a value equal to the necessary work of extraction. For elements of high atomic number the energy required is not obtainable by the methods available in the laboratory.

In an atom in equilibrium with a single electron, the centrifugal force on the latter equals the attraction of the nucleus. If there are several electrons, the electric force acting on an electron near the centre, in the K level, equals the attraction of the nucleus diminished by the resultant in the opposite direction, of the repulsions of $K - 1$ electrons, and the effect is thus an apparent diminution of the nuclear charge. The influence of the outer

electrons being practically negligible on account of their remoteness, matters proceed as if the Z elementary units in the nucleus were replaced by an apparent charge, Z_{app} .

The motion of the electron under consideration is then controlled by the same laws as given elsewhere for the hydrogen electron. Hence the total energy W is obtainable from the usual quantum condition, leading to the expression :

$$W = 2\pi^2 \frac{rme^4}{n^2 h^2} Z_{\text{app}}^2 = \nu_0 \frac{rh}{n^2} Z_{\text{app}}^2$$

where n is the quantum number corresponding to the orbit. For emission of radiation to occur, it is necessary for an external agency such as a cathode ray or an X-ray of sufficient *hardness*, to detach an electron from the K zone and transfer it to the outside of the atom. This results in the atom becoming unstable, and one of the electrons from the external levels falls in towards the centre to take the place of the departed electron. In this transition an amount of energy is emitted in the form of electromagnetic waves

of frequency ν determined by Bohr's postulate $\nu = \frac{\Delta W}{h}$. The value of ν increases with the atomic number, and is particularly large for transitions to the level closest to the nucleus. The emitted rays of highest frequency are thus the X-rays of the K series. When the passage of the electron towards the interior is arrested at the second orbit (which must have lost an electron) the X-rays emitted form the L series. It is because of the part they play in the production of the different X-ray series that the central orbits are denoted by the letters K, L, M, commencing from the innermost. Of the three lines α , β , γ of the K series, the first has the lowest frequency and arises by a transition from the L to the K level.

In discussing the frequencies emitted by an atom of hydrogen type, it was seen that they were all contained in the formula :

$$\nu = \nu_0 Z^2 \left(\frac{1}{n^2} - \frac{1}{m^2} \right).$$

In the present case, the quantum number n equals 1 for the K level and, for the $K\alpha$ line in particular, $m = 2$. As regards Z , it

has already been explained that for (Ze) must be substituted the apparent nuclear charge, which for the first level has the approximate value $(Z - 1) e$. From this we deduce that the frequency of the $K\alpha$ line *for any element whatsoever* should correspond to the formula

$$\nu = \nu_0(Z - 1)^2 \left(\frac{1}{1^2} - \frac{1}{2^2} \right)$$

or in the simplest form $\nu = A(Z - 1)^2$ where A is a constant.

This however is precisely the experimental result arrived at by Moseley in 1913! It will, in fact, be recalled (Vol. I, Chap. VI) that Moseley had found for the $K\alpha$ lines of various elements,

$$\nu_{K\alpha} = 82303 (Z - 1)^2.$$

The theoretical explanation of this result is now perfectly clear. It will be understood why it was stated at the time that the square root of the frequency was *almost* proportional to the atomic number. The above formula shows that only when Z has rather high values is the reduction of Z by unity without sensible effect. This correction (the reduction of Z by unity) was discovered empirically by Moseley, who also found for the coefficient A the value indicated by theory, a very striking result.

For the α line of the L series, Moseley gave the formula :

$$\nu_{L\alpha} = \frac{5}{36} \nu_0(Z - 7.4)^2,$$

in which the relationship between ν and Z is retained in the same form except for the empirical constant in the brackets, which now equals 7.4.

In the light of Bohr's theory, the reason for the increase in value of this constant can be readily understood. For the second level (the L level) it is obvious that an increase must occur because the constant represents the effect of a greater number of electrons occupying the central shells. Bohr's theory, treating the L series in the same way as a series of Balmer type with $n = 2$, $m = 3$, predicts :

$$\nu_{L\alpha} = \nu_0(Z - b)^2 \left(\frac{1}{2^2} - \frac{1}{3^2} \right) = \nu_0(Z - b)^2 \frac{5}{36}$$

which is precisely what Moseley found.

For X-ray frequencies also there exist the relations known as "combination laws,"* which affirm that by additive and subtractive combinations of levels which give rise to spectral series, other series of actually observed lines are obtained.

Between two levels III and I there exists a difference of energy which is given by the sum of the two differences (III — II) and (II — I), and as the frequency is always represented by $\frac{\Delta W}{h}$, the principle enunciated above clearly follows.

Case of Atoms more Complicated than Hydrogen

The problem of the motion of a single electron about a nucleus can be solved even when account is taken of the movement of the nucleus which, not having infinite mass, yields a little to the attraction of the electron. The problem is also soluble when the electron velocity is very high so that a relativity correction is necessary. Neglecting the relativity correction, a solution is obtainable if a magnetic or electric field is superposed on the nuclear field.

With the exception of hydrogen and ionised helium, however, all atoms possess more than one electron, so that, in general, we are confronted with a system consisting of three or more bodies. The resemblances between the spectra of hydrogen (and ionised helium) and the spectra of the other elements are sufficiently striking to lead to a search for the same kind of explanation of the spectral lines, in which the electrons are imagined as describing orbits selected from an infinity of possible orbits, by a quantum principle. Here, however, an unsurmountable difficulty is met with. The general problem of determining the orbits of three or more bodies, attracting or repelling one another in accordance with the inverse square law, remains insoluble despite all the efforts of mathematicians.

A large number of calculations have been made for helium, lithium and the alkali metals, but without any conclusive result. For the more complicated atoms too, if the problem could be

* Discovered by Ritz in 1908, five years before Bohr announced his theory.

formulated, the investigator would be faced with intractable mathematical difficulties. It must be remembered that the problem of three bodies has for many years occupied the attention of astronomers, many of them mathematicians of the first rank, without an exact solution in finite terms being obtained. For the particular case of helium, certain dynamically possible orbits have been determined and the corresponding energy values computed, but none of these models leads to the experimental value of the energy in one of the stationary states.*

It was supposed, for instance, that the two electrons of the helium atom in its normal state move in the same circular orbit, retaining at each instant their positions at the ends of a diameter. It is easy to write down the conditions for dynamical equilibrium and then to apply the quantum condition by Sommerfeld's method, putting the moment of momentum of each electron, or of the two together, equal to an integral multiple of $\frac{h}{2\pi}$. This seemed an

obvious generalisation of the system adopted with such success in the case of the hydrogen atom, but it led to a wrong value of the energy of the normal state. It was later supposed that the two electrons were disposed asymmetrically, then, that one electron occupied an outer orbit so that the energy values obtained were related to the stationary states of the ionised atom. Agreement with experiment was still not forthcoming. Further developments of theoretical physics have since demonstrated the futility of these efforts and have led to the abandonment of attempts to discover in the orbital construction of the atom the mechanism giving rise to spectral lines.

Interpretation of Optical Spectra. Arc and Spark Spectra

Lithium, sodium, potassium, rubidium and caesium are elements whose atoms easily relinquish an electron which is, as we say, loosely bound. Many facts combine to show that this is so. The outstanding evidence is the fact that the alkali metals have much

* In Chap. VIII. we shall see that the problem of the helium atom has been solved (1927) by the methods of wave mechanics.

lower ionisation potentials than any other elements in the periodic classification. Furthermore, in the periodic classification, the alkalis are the immediate successors of the rare gases (helium, neon, etc.), which are inert and devoid of chemical affinity. The explanation of the inert character of the rare gases is that their atoms are composed of a nucleus surrounded by electrons of which an outer group of eight exists in a particularly stable state, so that the ionisation potential acquires a value higher than that of other elements in the classification. After the rare gases there follow, in the ordinal arrangement, the respective alkali metals whose atoms as compared with the preceding gas atoms have acquired the additional valency electron situated at a great distance from the nucleus.

Such an electron, remote from the remainder of the atom (this remainder may be termed the "core"), experiences an attraction which equals that of the nuclear charge diminished by $(Z - 1)e$ because of the *screening* action of the external electrons. Thus it is permissible to consider the field acting on the valency * electron in a region relatively distant from the core, as identical with that which would exist if there were a single central charge e .

The central field, however, is much more complex, and a host of mathematical investigations have been devoted in vain to the study of the central orbits which the electrons must traverse in such a way that the corresponding energies agree with the values furnished by analysis of the spectra.

The atom of hydrogen consists of a nucleus forming the centre of a coulombian field in which the force varies inversely as the square of the distance, and, in analogous fashion, the atom of an alkali metal can be thought of as a central core surrounded by a force field which is nearly coulombian for the outermost electron which is responsible for the emission of light. This electron will move in certain orbits determined by the quantum conditions.

By analogy with hydrogen, an orbit is determined by a number

* The name owes its origin to the fact that in chemical reactions only this electron is concerned. The existence of only one such electron determines the monovalent character of the alkali metals.

k , the azimuthal quantum number, and a number n , the total quantum number. The only possible transitions are those for which k changes by unity, any transition for which k changes by two or more being forbidden. It was shown for hydrogen that the energy of the orbit depends only on the total quantum number n , and, having fixed n , there exist n orbits of the same energy which differ only in their eccentricities. To each of these corresponds an integral value of k ranging from 1 to n .

Thus for sodium, potassium, lithium, calcium and rubidium, the energy of the outermost electron, to which the emission of light is attributed, equals to a first approximation $-R\frac{h}{n^2}$.

If the analysis is pushed a stage further, however, it will be found that the energies of the n levels of total quantum number n differ a little one from another. To each principal level correspond a number of sublevels.

In systematic spectroscopy it is customary to indicate the levels for which $k = 1, 2, 3, 4$, respectively, with the letters s, p, d, f , so that the symbol $3p$, for example, means the level for which $n = 3; k = 2$. In every atom different successions of terms or levels have to be considered. There is a series of terms s for which $k = 1$ with $n = 1, 2, 3, 4 \dots$, then a series of terms p for which $k = 2$ with $n = 3, 4, 5$, etc. The scheme for sodium is given in the accompanying diagram (Fig. 13).

Not every pair of terms can be combined to give a spectral line because, by the selection rule, in a transition, the azimuthal quantum numbers of terms must differ by ± 1 , so that, for example, an s level can be combined only with a p term.

If the field in which the electron moves is nearly coulombian, it is clear that certain spectral lines of the alkali metals must be very close to those of hydrogen. The lines for which this is the case will be those deriving from rather high quantum numbers.

For example, the three orbits of an alkali defined by $n = 5, k = 5; n = 6, k = 6; n = 7, k = 7$, are three circles which correspond to stationary states almost identical with those of hydrogen, and it may be inferred that if the stationary states of an alkali and of hydrogen are arranged in order of decreasing

energy, the two systems will progressively approach. This, in fact, is confirmed by experiment, with a certain limitation which will now be indicated. The various radiations are emitted only in transitions between two stationary states for which the azimuthal quantum numbers differ by unity, as required by the selection rule which will be discussed in Chap. III. In other words, the

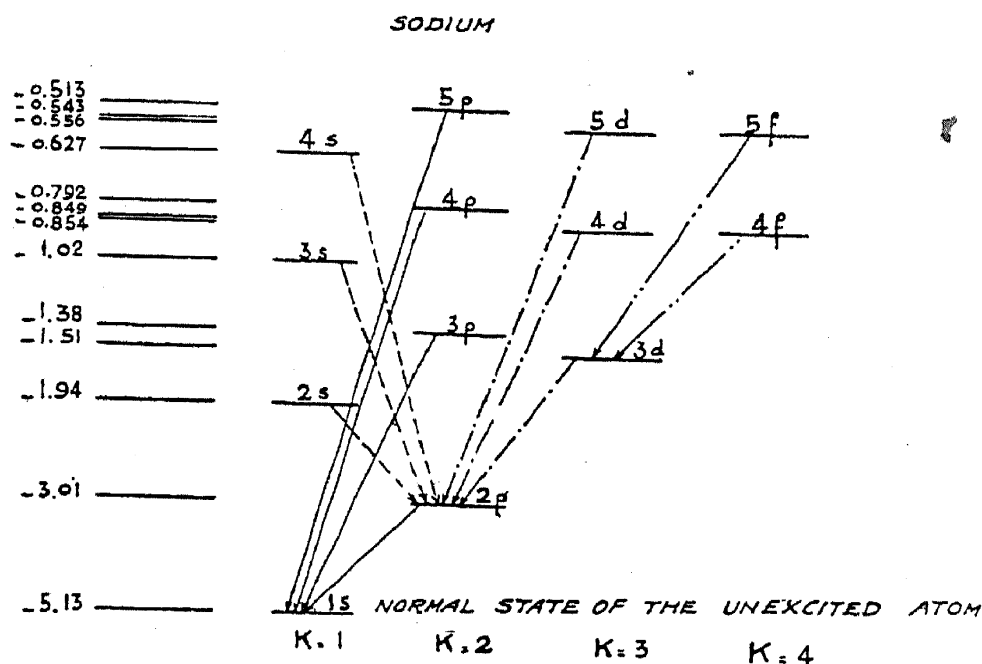


FIG. 13.

principal series*	_____
sharp „	-----
diffuse „
Bergmann „

only transitions possible are those for which $\Delta k = \pm 1$. Up to this point, reference has been made to orbits characterised by rather high total quantum numbers, but the other quantum

* The *principal series* consists of transitions for which the final state is (1, s) the consecutive lines of the series corresponding to the electron jumps : (1, s) \rightarrow (2, p) (1, s) \rightarrow (3, p) (1, s) \rightarrow (4, p) and so on.

The general symbol is : (1, s) \rightarrow (m, p).

Two series have as terminal state (2, p). One comprises transitions from s states, and is termed the *sharp series* with the general symbol (2, p) \rightarrow (m, s). The other is generated by transitions from the various d levels, giving the so-called *diffuse series* with the general symbol (2, p) \rightarrow (m, d).

Finally, the *Bergmann series* is represented by the general symbol (3, d) \rightarrow (m, f) denoting transitions terminating on the (3, d) level.

Many other series occur, but those named are specially important in spectroscopy, and therefore also in astrophysics.

number k on which the eccentricity depends, was left unspecified. Since for a given value of n , *i.e.*, a given value of the energy, there are n possible orbits, more or less elongated, and since the more eccentric of these approach very close to the nucleus at perihelion, the above statement that for large values of n the terms of sodium tend to coincide with those of hydrogen, is more nearly true, the higher the series considered, that is to say, for terms of high k value. This is verified in practice.

After these general considerations we proceed to show how a theory of an approximate character enables us to explain the series which the early spectroscopists had identified in the spectra of the elements.

Consider an atom of atomic number Z . We suppose that $Z - 1$ electrons occupy a small central region, the remaining electron being situated rather farther out. The atom can then be regarded as a spherical distribution of negative electricity surrounding the nucleus, plus an external electron subjected to the action of the nucleus and the $(Z - 1)$ electrons. The latter diminish the field of the nucleus to a varying extent depending on the position in the field of the point considered. If the *external* electron which is in motion penetrates into the interior of the atom approaching to a point distant r from the nucleus, the screening action will no longer equal $(Z - 1)e$, but will be given instead by $(Z - \alpha)e$, where α is the number of electrons contained in the sphere of radius r .

Thus, in passing from hydrogen to the other atoms, we are presented with the primary problem of computing the stationary states or energy levels W of an electron subject to a non-coulombian force. To represent the latter analytically, it is recalled that the coulombian potential due to a charge e has the value $\frac{e}{r}$. The field in the present case must correspond to a potential $U(r)$,

which at large distances tends asymptotically to the value $\frac{e}{r}$. Hence developing $U(r)$ in series according to powers of r , we shall have to a first approximation :

$$U(r) = \frac{e}{r} + \frac{b}{r^2} + \dots$$

where b is a constant.

The electric force equals $-\frac{\partial U}{\partial r} = \frac{e}{r^2} + \frac{2b}{r^3}$, and the field is therefore defined at all points, and we can pass to the calculation of the orbit described by the electron. Adding the kinetic energy to the potential energy, the total energy of the orbit is obtained. The orbit is found to be an unclosed curve which in fact is a *rosette* similar to that shown in Fig. 8. Introducing at this point Sommerfeld's quantum conditions :

$$p = mr^2\dot{\theta} = \frac{h}{2\pi} k$$

k = azimuthal quantum number

$$\int m r dr = n_r h$$

n_r = radial quantum number

all the stationary, or preferred, orbits are isolated, forming a doubly infinite array specified by the two parameters k and n_r . The energy W of each orbit is in this way definitely fixed, and we obtain the *Rydberg formula*

$$W = -\frac{Rh}{(n - \alpha_k)^2} \quad \text{where } \alpha_k = k \left[1 - \sqrt{1 - \frac{8\pi^2 b e m}{k^2 h^2}} \right]$$

R is Rydberg's constant and n is the total quantum number. It is seen, therefore, that the spectral terms of an alkali metal take values of the type

$$\frac{R}{(n + a)^2}$$

An improved theory modifies the above and yields the Ritz formula for the spectral terms :

$$\frac{R}{\left(n + a + \frac{\alpha}{n^2}\right)^2} \quad \text{where } a \text{ is always negative and } \alpha \text{ is always positive,}$$

and both a and α depend only on the azimuthal quantum number.*

Thus a and α have the same values for all s terms, the same values for all p terms, etc.

For further details of these calculations the reader is referred to Fermi's "Introduzione alla Fisica atomica," or Andrade's "The Structure of the Atom."

The expression for the energy just obtained is a very important result. Comparing it with the analogous expression for hydrogen,

$$W = -\frac{Rh}{n^2},$$

we observe at once that the spectrum of any atom

whatever should contain series analogous to the Balmer series of hydrogen, corresponding to fixed k and varying n . But a further infinity of frequencies (knowing the energies W , the frequencies

are also determined because $\nu = \frac{\Delta W}{h}$) will arise by varying k ,

keeping the total quantum number n constant. This scheme includes to a first approximation, the entire spectrum of an atom, and experiment confirms the prediction of the Rydberg formula. Actually accurate analysis of the innumerable lines constituting a spectrum, the frequencies of which appear at first sight distributed at random, had shown many years earlier (1890) that in many cases grouping of lines into series could be effected by observing the *character of the lines*. Thus some lines appear sharp or indistinct or diffuse. In addition, a physical change, involving the spectrum, affects certain lines similarly, those in fact which belong to the

* a is termed the Rydberg correction, α the Ritz correction.

same series. For example, a magnetic field splits every line of a given series into several lines in an exactly similar way. If one line is broadened by compressing the emitting gas, the companion lines are broadened at the same time. Thus the formal characteristics of the spectral lines lead naturally to classification in series, which are the same whatever characteristic be taken as

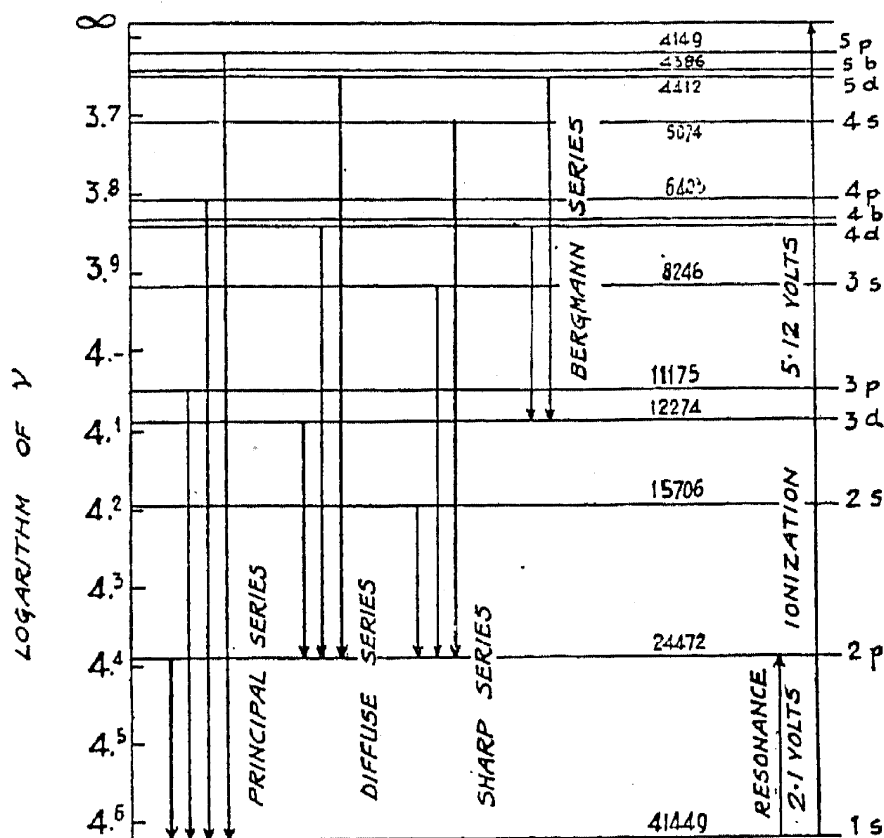


FIG. 14.—Schematic Representation of the Arc Spectrum of Sodium.

criterion. These series are to a first approximation explained by the Rydberg formula.

The frequencies of all the most important lines are obtainable, as shown in Fig. 14, by the following transitions, bearing in mind that the latter can only occur between contiguous columns.

Transition	$p \rightarrow s$.	.	.	principal series.
„	$d \rightarrow p$.	.	.	diffuse series.
„	$s \rightarrow p$.	.	.	sharp series.
„	$f \rightarrow d$.	.	.	Bergmann series.

The lines generated by transitions $s \rightarrow p$ are the most intense.

In Fig. 14 the series of sodium are again represented, this time in terms of the wave numbers, so that, taking the difference of

these for two different levels, we obtain directly the wave number of the emitted radiation.

The fine structure is not indicated in this scheme and the numbers of the levels are therefore subject to this emendation.

Considering now a singly ionised atom, it is clear that the optical electron which in the neutral atom was subject to the effective nuclear charge $Ze - (Z - 1)e = e$, will now move in an approximately central field, but of effective nuclear charge $Ze - (Z - 2)e = 2e$. Repeating the derivation of the spectral terms already given, it is only necessary to change the value of the central charge to obtain for the ionised atom the expression

$$n_k = \frac{4R}{(n - \alpha_k)^2},$$

where α_k is a constant for the same succession of terms. Similarly, for the doubly-ionised atom, one arrives at the formula,

$$n_k = \frac{9R}{(n - \alpha_k)^2},$$

and so on. These formulæ give approximately the terms in the spectra produced in the electric spark, where the disruptive action of the discharge is known to ionise the atoms.

It is important to mention that in the spark spectrum arc lines also appear, and *vice versâ*.

Structure of Molecules

It was not possible to solve the problem of the helium atom by applying Bohr's theory and Sommerfeld's conditions, and it is not surprising therefore that no success has been attained in the analogous problem for molecules. Not even for the simplest molecule, hydrogen, has it been possible to determine the electron orbits. Here, too, laborious calculations were made but without success. In the face of these failures (1923—1924) physicists became disturbed and doubts arose as to the adequacy of the quantum rules which, it must be admitted, had been suggested merely as tentative proposals, a little artificial, and justifiable only by the correctness of the conclusions drawn from them.

Of course, the successes attained gave grounds for believing that Sommerfeld's conditions must contain some fundamental element

of the truth, but the principles from which they followed remained undiscovered. The latest developments in this direction we shall see in wave mechanics and quantum mechanics.

Returning to the problem of the hydrogen molecule, mention must be made, because of its historical importance, of a model given by Bohr in 1913. This consists of two nuclei separated by a distance $2a$. In the plane perpendicular to the joining line the two electrons move in a circular orbit of radius b . As the charges are known, the conditions of equilibrium of such a system can easily be found, by writing down first the condition for the nuclei to be at rest under the action of their mutual repulsion and the attractions of the electrons, and then the conditions for the resultant inward attraction on the electrons, to equal the centrifugal force.

Finally the quantum condition must be applied :

$$mv \times a = \frac{h}{2\pi}.$$

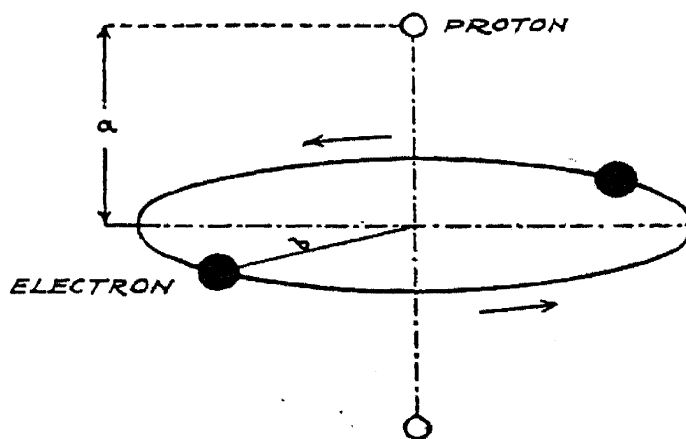


FIG. 15.

The three equations obtained fix a , b and v , and the system is completely determined. On calculating the energy required to dissociate this Bohr molecule, we obtain, for a gramme molecule, the value 60,000 calories, whereas experimental determinations by various investigators give a result in the neighbourhood of 90,000 calories.

Moreover, each molecule constructed on this plan represents an elementary magnet which, in a magnet field, must be orientated in the direction of the lines of force. Hydrogen would therefore be paramagnetic. Actually it is diamagnetic. For these and other reasons the model had to be abandoned.

Elastic Collisions between Electrons and Atoms. Elastic Collisions between Atoms

We consider the process which takes place when an electron stream of controllable kinetic energy passes through a gas. The

experimental arrangement consists essentially of an anode plate facing a metallic net or grid which can be raised to different potentials. Behind the grid is a filament which can be heated and serves as a source of electrons. The whole is enclosed in a glass bulb containing the gas to be examined. Alternatively a fragment of metallic sodium or other volatile metal may be placed in the bulb, to be subsequently heated and vaporised, enabling the properties of the metallic vapour to be studied.

The filament is first raised to incandescence and emission of electrons ensues. The emitted electrons are suitably accelerated by the potential of the grid and emerge to bombard the gas or vapour under examination. It may happen that the kinetic energy acquired by these projectiles in the accelerating field is sufficient to wrest an electron from the atom of sodium, or generally of the element under test. Ionisation then occurs and is revealed by the abrupt increase of the current passing through a galvanometer in the plate circuit. Before the accelerating field is sufficiently high for ionisation to occur, another phenomenon may be observed, the atoms struck being raised to an excited state with subsequent emission of light. A discussion of this phenomenon will be given in the next section.

For the present, however, we confine our attention to the case in which the accelerating potential is so low that the electrons possess insufficient energy to produce either excitation or ionisation of the atom with which they collide, and are merely thrown back by the impact.

We are thus led to the study of so-called *elastic collisions*. The electrons and also the atoms taking part in such collisions behave as smooth, perfectly elastic, spheres.

The characteristic of an elastic collision is that the momentum (the vector quantity *) and the kinetic energy of translation are both conserved. If the colliding particles have energy other than that associated with their translational motion, *i.e.* internal energy or rotational energy, in an elastic collision no conversion of this energy into kinetic energy of translation or *vice versa* occurs.

The equations governing elastic collisions are three in number,

* Hence, conservation implies that the three velocities U , v , V lie in a plane.

and are very simple, particularly if the particle struck is initially at rest.

The first states that the kinetic energy after the collision, $\frac{1}{2}Mv^2 + \frac{1}{2}mV^2$, equals the kinetic energy $\frac{1}{2}mU^2$ of the impacting body,

$$\frac{1}{2}mU^2 = \frac{1}{2}Mv^2 + \frac{1}{2}mV^2. \quad (1)$$

v , M , being respectively the acquired velocity and the mass of the originally stationary sphere.

Conservation of momentum leads to two further equations. If θ is the angle between the original velocity of the impacting particle

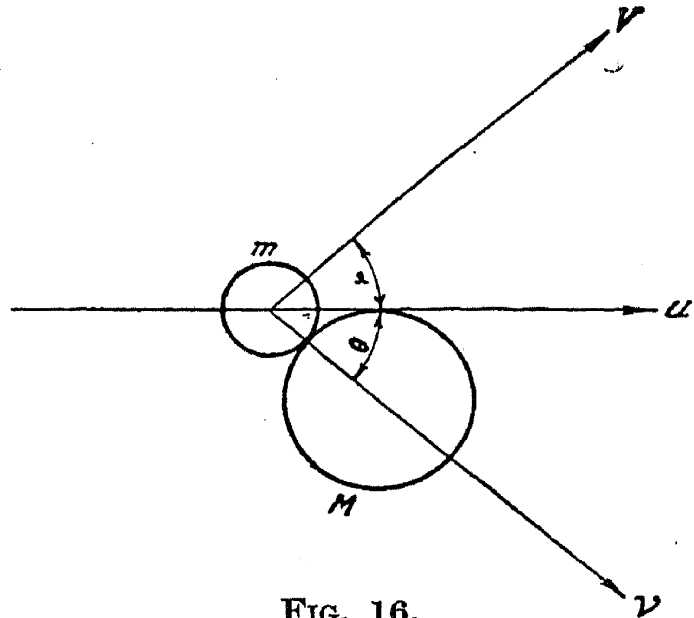


FIG. 16.

m , and the velocity acquired by the stationary atom M and ϕ is the angle between the initial and final velocities of the sphere m (atom or electron), the two relations are as follows :

momenta resolved along the direction of U

$$mU = mV \cos \phi + Mv \cos \theta \quad . \quad . \quad . \quad (2)$$

momenta resolved perpendicular to the direction U

$$0 = mV \sin \phi + Mv \sin \theta \quad . \quad . \quad . \quad (3)$$

These three equations contain three velocities, two angles and two masses, in all seven quantities. But actually the two angles θ and ϕ do not change if the ratios $\frac{m}{M}$, $\frac{U}{V}$, $\frac{v}{V}$ remain constant. In other words, there are five not seven independent quantities in the equations. In fact, the equations may be written,

$$\frac{1}{2} \frac{m}{M} \frac{U^2}{V^2} = \frac{1}{2} \frac{v^2}{V^2} + \frac{1}{2} \frac{m}{M} \quad . \quad . \quad . \quad (1')$$

$$\frac{m}{M} \frac{U}{V} = \frac{m}{M} \cos \phi + \frac{v}{V} \cos \theta \quad . \quad . \quad (2')$$

$$0 = \frac{m}{M} \sin \phi + \frac{v}{V} \sin \theta. \quad . \quad . \quad (3')$$

Knowing the values of the two angles θ and ϕ , these three equations suffice to determine $\frac{m}{M}$ the ratio of the masses.

This result having been established, we recall Wilson's method of photographing particle trajectories obtained in a "cloud" confined in a transparent walled chamber. Let the colliding particles be rapidly moving helium atoms (α -particles emitted by radioactive substances), bombarding the atoms of a gas, say, hydrogen or helium. Among the photographs taken will be some in which, in addition to the rectilinear tracks of the incident ion-producing α -particles, a characteristic Y-shaped trajectory is observed, corresponding to a collision between an α -particle and an atom. By determining the two angles θ and ϕ , which can be done by taking photographs simultaneously in two directions at right angles, the ratio $\frac{m}{M}$ of the masses concerned, is determinable and serves as a check on the theory of elastic collisions.

In this way Blackett * deduced, as the result of thousands of photographs, $\frac{M}{m} = 0.981$ (practically unity) from the trajectories of α -particles in helium ($\frac{M}{m} = 1$) and, from the bifurcated tracks in hydrogen, $\frac{m}{M} = 0.253$, which is sensibly the same as the known ratio of the mass of the hydrogen atom to that of the α -particle, $\frac{1}{4}$.

Turning to another aspect of the problem, the energy given up by the impacting body, we suppose the latter to be an electron emitted in the apparatus mentioned above. It is easy to show that the ratio of the maximum amount of energy given up, to the initial energy, has the value

$$\frac{E_{\max}}{E} = \frac{4M}{(M + m)^2} \cong \frac{4m}{M} \cdot \cdot \cdot \cdot \cdot (*)$$

The approximate value $\frac{4m}{M}$ is sufficiently exact when $\frac{m}{M}$ is less

* See *Proc. Roy. Soc.*, 107, p. 349, 1925.

than 0.0006, which is the case in practice because the electronic mass is 1,840 times smaller than the mass of the hydrogen atom and $\frac{m}{M_{\text{hyd}}} = \frac{1}{1840} \cong 0.0006$. In the case of all other atoms the ratio is even smaller.

Evaluating the *average value* of the energy actually transferred, the result comes out to be just *one-half the maximum value* given above.

Consider a stream of electrons accelerated through a gas by means of a fall of potential between two opposing electrodes. Owing to the presence of the gas, the electrons arrive at the anode with less energy than corresponds to the potential drop, even though the latter is so small that the electrons are unable to excite or ionise the gas atoms. The average number of collisions sustained by an electron in its path, can be calculated. It involves, however, a far from simple statistical analysis, because account must be taken of the fact that the atoms are in a state of thermal agitation and the kinetic energy of the electron increases as it moves forward in the electric field.

K. T. Compton and H. Herz performed the calculation of the energy lost by an electron in its path. The result depends, as is obvious, on the radius of the atoms and also on the ratio $\frac{m}{M}$, since the average amount of energy lost in a collision equals $\frac{1}{2}E_{\text{max}} = 2E\frac{m}{M}$, from (*) above.

The theoretical result was verified experimentally in some delicate experiments by Compton and Benade, details of which must be passed over here.

The conclusion is that the transfer of energy from a slowly moving electron to an atom of helium, mercury, etc., is exceedingly small in amount, in sharp contrast to the state of affairs which obtains when the velocity of the electron exceeds a certain critical value. When a monatomic gas is bombarded with a stream of electrons of kinetic energy in excess of the critical value, a certain number of the electrons lose by collision much larger amounts of

energy than those just computed. Such collisions are termed *inelastic collisions*.

In the following three sections, inelastic collisions and the phenomena they bring about, *excitation* and *ionisation*, will be discussed.

The methods of inducing the atom to radiate, available to the physicist, may be classified under three heads :

(1) Collisions of electrons, *i.e.*, bombardment of a solid or gaseous substance by accelerated electrons. If the difference of potential accelerating the electrons is of the order of several volts, the substance emits only visible radiation, but X-rays are obtained with potential differences ranging between a few hundreds and hundreds of thousands of volts. Whatever the experimental conditions, the spectrum of the radiation produced is always characteristic of the emitting substance.

(2) Rise of temperature.

(3) Irradiation of the substance with light or X-rays.

Excitation and Ionisation of Atoms. Thermal Excitation

It has been seen in the case of the spectrum of hydrogen, the simplest of the atoms, that an electron can leave its orbit to move temporarily into a more external orbit. It is better to say the electron can pass to a higher energy level, as the reference to orbits ties us down too closely to the model. More generally, any atom is excited when one of its electrons is raised to a higher energy level, just as though we were dealing with a weight which could be raised or lowered. The excitation of an atom requires therefore the introduction of energy. On the other hand, when the atom returns to its normal state, energy is liberated. As shown by experimental spectroscopy, the number of different levels to which a particular electron can be raised is very great.

Among these, one stands out as being of particular interest, namely, the level which requires with respect to the normal level the smallest increment of energy. In practice this increment is termed, in a restricted sense, the *resonance energy*.

It is evident that excitation of the atom concerns the less

strongly bound electrons, which occupy the periphery and which take part in chemical combinations, and are for this reason termed valency electrons. These electrons are responsible for the emission of the spectral lines. This agrees with the fact that, in the visible region of the spectrum, the amount of energy necessary for excitation is a thousand times smaller than in the X-ray region, so that the optical lines can only be due to these loosely-held peripheral electrons which can be displaced with the expenditure of a relatively small amount of energy.

The excited state of the atom is unstable, for after a very brief sojourn, which measurements by Wien and others show to be of the order 10^{-8} sec., the atom returns to the normal state, the return being accompanied by the emission of a quantum $h\nu$ of monochromatic light of frequency $\nu = \frac{\Delta W}{h}$, given by the quotient of the emitted energy by Planck's constant. Whether this "quantum" is a true particle of energy $h\nu$, just as a particle is, is a question we shall touch upon later.

The excitation of an atom and, more generally, the passage from an already excited state to a state of higher excitation, can be affected not only by the absorption of radiation of frequency ν where $h\nu$ equals the necessary increment of energy, but may also occur in a collision or by the action of heat.

If we consider, for simplicity, a monatomic gas, say, a metallic vapour or a rare gas, in which the atoms or molecules are single, we can imagine that the translational energy evaluable by the kinetic theory may be sufficient at high temperatures for mutual collisions to evoke the phenomenon of light emission. This effect is the thermoluminescence actually observed.

Since, at ordinary temperatures, the kinetic energy of atoms is very small compared with that required for excitation, we shall not expect to observe emission of light in a gas unless the latter is excited by electron bombardment or irradiation.

For the alkali metals, the excitation energies lie between 2×10^{-12} and 3×10^{-12} erg, the lower limit referring to caesium. For the elements of the second group of the periodic system the excitation energy amounts to two to three times that of caesium. For lead,

it is again about equal to that of cæsium. The corresponding spectral lines (the resonance lines) lie in the visible region for the alkalis, magnesium, calcium, strontium and barium, and in the ultra-violet for zinc, cadmium and mercury.

The average kinetic energy possessed by a molecule of a monatomic gas is known by the kinetic theory to be $\frac{3}{2} \frac{R}{N} T$. At ordinary temperatures, that is, in the neighbourhood of 300° absolute, this equals 5.6×10^{-14} erg, since $\frac{R}{N} = 1.37 \times 10^{-16}$. The kinetic theory also establishes the statistical distribution of velocities (Maxwell's law) and kinetic energies. The fraction of molecules with translational energy x or more times the mean value given above, is deduced to be e^{-x} . Thus, since 2×10^{-12} erg is required to excite the cæsium atom, x must be very large and the corresponding probability of molecules existing with such velocities is absolutely negligible.

On the other hand, at temperatures of $1,200^\circ$ C., *i.e.*, $1,500^\circ$ absolute, it is sufficient for x to equal 6, and one molecule in every 400 will have the necessary energy. Thus it is clear why at ordinary temperatures the proportion of atoms which possess sufficient energy to excite other atoms by collision, is insignificant, whereas at $1,200^\circ$ C. the proportion is sufficiently large to produce a perceptible luminescence.

When at high temperatures a vapour begins to radiate, the first spectral line observed corresponds to transitions from the lowest excited level to the normal state. As the temperature rises above this limit, the translational motion becomes increasingly violent and is able to produce higher excitation, so that new spectral lines appear.

The energy necessary to remove completely a valency electron from the atom, the value of which can be deduced from spectroscopic observations and by other methods, is termed the ionisation energy.

For the alkali metals, and also for the elements of the second group of the periodic system, the ionisation energy is two or three times the excitation energy.

The *ionised atoms* can, in their turn, be excited just as neutral atoms, by the transfer of a valency electron to a higher level. In this way the elements give, in addition to the spectral lines of their neutral atoms, other lines due to the ionised atoms, the latter naturally requiring more “energetic” conditions for their production.

The lines of the neutral atom are formed in the electric arc, the lines of the ion in the spark discharge. It is observed that the spark spectrum of an element of atomic number $Z + 1$ closely resembles the arc spectrum of the element with atomic number Z , in agreement with the latter having one fewer peripheral electron than the former (Sommerfeld and Kossel, 1919).

Excitation and Ionisation Potentials obtained by the Electron Collision Method. Collisions of the Second Kind

Bohr's theory of atomic structure provided, as we have seen, the key to the explanation of spectra. It was based on the following two assertions : (a) the internal energy of the atom can assume only well-defined discrete values, and (b) the frequency of the radiation emitted in the transition from one energy level to

another equals $\nu = \frac{\Delta W}{h}$. The theoretical explanation of the phenomena of spectra results from the combination of these two fundamental postulates. It was therefore a great step forward in atomic physics when, in 1913, Franck and Hertz succeeded in *confirming directly the former of these two postulates*, by a method which did not depend in any way on the truth of the latter.* This they were able to do by investigating collision phenomena between atoms and free electrons, the electrons emitted by a glowing filament being passed through a gas or vapour. Ionisation potentials had been determined in a similar way by Lenard in 1903. The following is an account of his method which we have already had occasion to refer to previously.

A metal plate L (Fig. 17) serves as a source of electrons when subjected to the action of ultra-violet light. Facing this plate is

* A complete description of investigations of this kind is to be found in the “Handbuch der Physik,” Vol. XXIII, Chap. 7,

a positively charged metal gauze the potential V of which can be varied as desired. On the other side of the gauze T , and at a potential lower than that of T by a fixed amount V^1 , is placed an electrode connected to an electrometer E . Thus there is a retarding potential V^1 between T and E , and V^1 is chosen so large that no electron passing through the gauze can reach the electrode. If, however, the accelerating potential V between L and T surpasses a certain limit, the ionisation potential, the electrons which pass through the grid possess sufficient energy to ionise the molecules with which they collide and the positive ions produced are collected by the electrode E and recorded by the electrometer. Plotting the positive deflections of the electrometer for different

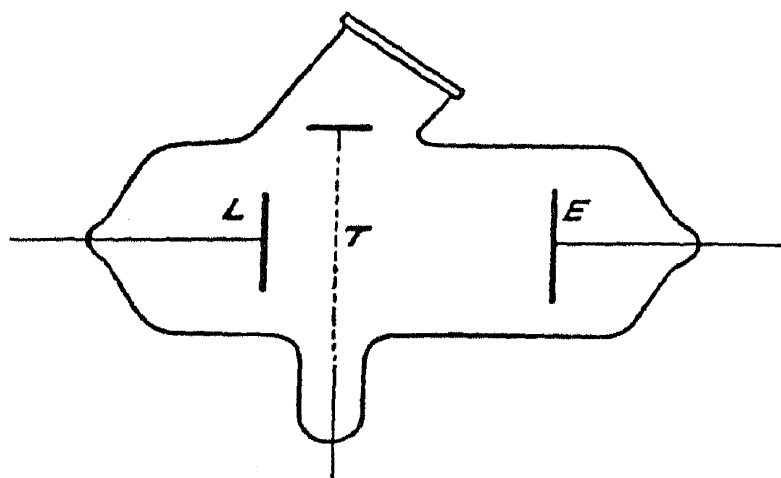


FIG. 17.

accelerating potentials against the corresponding values of the latter and extrapolating the curve to cut the abscissa, the ionisation potential at which positive ions begin to be produced is at once obtained.

The phenomenon of electron collision yields valuable and unambiguous

results because, in the first place, the kinetic energy of an electron is known exactly from the difference of potential employed to accelerate it, and, secondly, because the mass of the electron is negligible compared with that of the atom, and the whole of the electron energy is lost in the collision. In effect, it can be assumed that the electron energy has *all* gone to increase the internal energy of the atom concerned in the collision. This represents a very great simplification.

So long as the kinetic energy of the electron is small compared with the energy required to excite the atom, the electron suffers no loss of energy in the collision. The electron then rebounds like a billiard ball reflected from the cushion. This case comes under the heading of elastic collisions. The electron alters the direction

of its motion, its velocity is slightly changed, and the atom struck undergoes no internal change. The details of this process have already been discussed. It should be noted that elastic collisions occur only in the case of monatomic gases, that is to say, for the rare gases or metallic vapours.

Inelastic collisions, in which the colliding electron loses energy, are possible when the accelerating is raised to a value V such that the product Ve equals the excitation energy of the atom, ΔW .

The atom then emits monochromatic radiation $\nu = \frac{\Delta W}{h}$ in returning from the excited to the normal state, the frequency being determined by Bohr's relation which, in this case, can be written $\nu = \frac{Ve}{h}$. Remembering that $\lambda = \frac{c}{\nu}$, and substituting the known values of h , e and c , this result takes the form

$$\lambda V = 12340,$$

where V is expressed in volts, λ in Ångström units. For the elements of the first group of the periodic system, λ is the wave-length of the resonance line. For the elements of the second group—for which there are two resonance lines of considerably different wave-lengths—two resonance potentials have to be considered.

For many elements *direct determinations* of excitation potentials have been made, with the aid of suitable apparatus in which electrons of variable velocity are passed through the gas or vapour and the resultant current measured with a galvanometer.

If the values obtained for the current are plotted against the accelerating potential V , which imparts an amount of energy Ve to each electron, the resulting curve shows a pronounced discontinuity at the value of V for which inelastic collisions occur. The experiment represents a remarkable confirmation of Bohr's condition determining the frequency, which is in fact found to satisfy the relation $\nu = \frac{Ve}{h}$.

It may be desirable to show why the experimentally determined kinetic energy of the electron can be taken in practice as equal to the energy adsorbed

internally by the atom. If M is the mass of the atom and V its velocity after the collision, m the mass and u the initial velocity of the electron, conservation of momentum requires that $mu = MV$. The energy T absorbed by the atom is given by the equation :

$$K = \frac{1}{2} mu^2 = \frac{1}{2} MV^2 + T,$$

and it follows that,

$$T = K \left(1 - \frac{m}{M}\right).$$

As the mass of the atom may be anything from 1,845 times to about half a million times greater than that of the electron, the latter expends more than (999/1,000)ths of its energy in exciting or ionising the atom. The assumption that the energy of the electron can be taken as the excitation or ionisation energy is therefore justified.

In the case of mercury (see Fig. 18), Franck and Herz observed the first inelastic collisions at 4.9 volts, and, at the same potential,

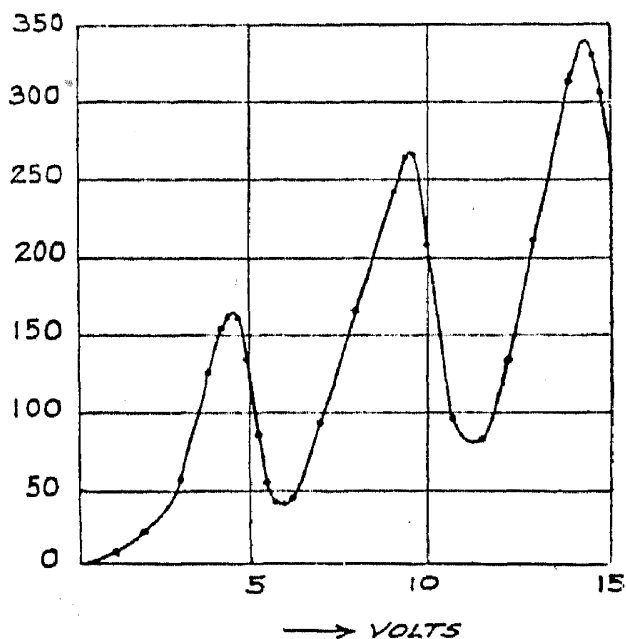


FIG. 18.

emission of the resonance line $\lambda = 2536 \text{ \AA}$ commenced. Subsequent measurements led to a somewhat lower value of V (4.8), and it is easily verified that

$$\frac{12340}{2536} = 4.8.$$

The curve obtained (Fig. 18) shows a succession of maxima. Beyond the first critical potential, the current transmitted sinks to a low value. As the accelerating potential is increased, the region of space in which the inelastic collisions occur moves towards the

electron emitting filament. The electrons which have lost their kinetic energy in a collision are subject to further acceleration, and some of them penetrate to the collecting electrode and the current increases. Finally, a sufficiently high value of the potential is reached for the electrons to undergo two inelastic collisions and the current falls. With further increase of the accelerating potential the process is repeated, and so on.

If there are two resonance states, as is the case for the metals of the second group, we should find a second potential such that the product Ve equals the product $h\nu$ where ν is the frequency of

another radiation emitted. The determination of critical potentials as close together as in this case, involves serious experimental difficulties, and has not yet been accomplished save in the case of mercury. It is however easy to determine the ionisation potential which must also conform to the relation $\lambda V = 12340$.

For mercury the ionisation potential equals 10.38 volts and the light emitted has wave-length $\lambda = 1188 \text{ \AA}$.

A similar confirmation of the Bohr principle has been obtained, both in respect of the resonance potential and the ionisation potential, for many other elements. Values of the resonance potentials and ionisation potentials for a number of elements in the first two groups of the periodic system are given below.

Excitation and Ionisation Potentials in Volts. (Foote and Mohler.)*

Alkali Metals.

				Sodium.	Potassium.	Rubidium.	Cæsium.
<i>Excitation Potential</i>	Cal.	.		2.09	1.61	1.6	1.44
	Obs.	.		2.12	1.55	1.6	1.48
<i>Ionisation Potential</i>	Cal.	.		5.12	4.32	4.16	3.88
	Obs.	.		5.13	4.1	4.1	3.9

Metals of the Second Group.

				Magnesium.	Calcium.	Zinc.
1st <i>Excitation Potential</i>	Cal.	.		2.7	1.88	4.01
2nd " "	"	"	.	4.33	2.92	5.77
<i>Ionisation</i>	"	"	.	7.61	6.09	9.35

The observed values approximate closely to those given above.

* Note that the potentials may be expressed either in volts or in absolute units. The connection between the erg and the volt is obtained from the relation

$$\text{energy} = \frac{1}{2} mv^2 = Ve$$

which leads to the result, 1 electron volt = 1.591×10^{-12} erg.

Davis and Goucher's apparatus for experiments of this kind is shown schematically in Fig. 19.

G is an electrically heated filament. The thin central portion is at red heat and emits electrons. T is a wire gauze, Z a plate connected to an electrometer E. A potential difference V_1 is applied between G and T, giving a field which accelerates the electrons towards Z. Facing the plate Z is another metallic gauze T', this representing the improvement over the apparatus of Lenard and Franck and Herz.

Between T and T' the electric field V_2 is retarding, whilst

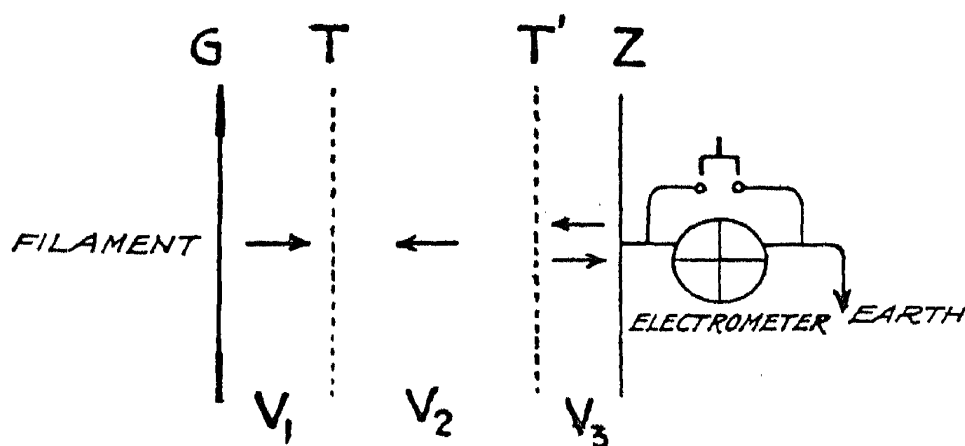


FIG. 19.

between T' and Z is a *weak* field V_3 whose direction can be reversed, as shown by the arrows in the figure.

The electrons arrive in the space included between the two metal gauzes and collide with gas molecules. The latter are excited and emit ultra-violet radiation. The radiation falls on T' and Z and photoelectrons are emitted. If V_3 is directed towards the left the plate acquires a positive charge, but if V_3 is reversed, the photoelectrons from Z are unable to escape and those from T' are collected by the plate which then acquires a negative charge. Thus, changing the sign of V_3 reverses the electrometer deflection. Suppose now that between the gauzes *ionisation* is occurring. The positive ions produced are driven by the field, through T' onto the plate Z, and this will occur *whichever* the direction of V_3 , because V_3 is very small compared with V_2 . Reversing V_3 will now leave the direction of the electrometer deflection unaltered.

In this way it is possible to distinguish between ionisation and excitation of the gas atoms.

Up to the present our discussion has been confined to excitation produced by electron collision. But if electrons of energy $\frac{1}{2}mv^2 = Ve$ bring about the emission of radiation ν such that $\nu = \frac{Ve}{h}$, the atom can be similarly excited by energy in the form of radiation of frequency ν . This is the phenomenon of *resonance*, a name borrowed from wave theory. Thus, the mercury atom can be excited by receiving, from an electron, energy equivalent to 4.9 volts, and it can also be excited by radiation of wave-length $\lambda = 2536 \text{ \AA}$. If a beam of light of this wave-length is passed through mercury vapour, the latter *responds* by emitting the same light in all directions. Similarly, the vapour of sodium, which emits the line $\lambda = 3303$, will reradiate light of this wave-length, and so on.

When a gas is irradiated with light of frequency greater than the resonance frequency, the return of the atom from the excited state to the normal may occur *in stages*. This is the phenomenon of *fluorescence*. In fluorescence, as the energy difference $W_1 - W_2$ is subdivided into two steps, two new frequencies are generated both lower than the resonance frequency $\frac{W_1 - W_2}{h}$. Thus a vapour illuminated with light corresponding to one of its absorption lines, may in certain cases diffuse, in addition to the resonance radiation of the same frequency as the incident light, other lines in its spectrum, these having in every case frequencies less than that of the incident light. This is the substance of the law laid down by Stokes in 1852, which applies to substances in general and not only to gases.

The discussion of excitation and ionisation given here has been limited to the merest outline. We mentioned above the investigations of Franck and Herz (1913–1914), who, apart from

Lenard, were the first to carry out researches on this subject, but since their work many other physicists have devoted themselves to this field, among whom may be mentioned particularly Davis and Goucher, K. T. Compton, Foote and Mohler, Bazzoni, Knipping, Einsporn, Millikan and Wood.

Mercury vapour has been the object of special study. It possesses an ionisation potential of 10.3 volts. There are a number of excitation potentials (or *radiation* potentials as they are called by some English writers), the lowest being at 4.68 volts. The others occur at 4.9, 5.47, 5.76, 6.73, 7.73 and 8.64 volts respectively. These potentials, determined experimentally from the abrupt inflexions in a curve of the type described above, each correspond to a spectral line of the substance, of frequency ν given by the relation $eV = h\nu$.

In addition to ionisation potentials in the strict sense, so-called *second order ionisation potentials* have been determined experimentally for some atoms. These correspond to the removal of the second of the two least strongly bound electrons of the atom. Magnesium, for example, has the two ionisation potentials 7.61 and 15 volts, helium 24.5 and 78.6 volts.

Closely related to the topic of the present paragraph is the question of *inelastic collisions between atoms*, to which a few words will now be devoted.

We know that when an electron of kinetic energy greater than the resonance potential collides with an atom, it can transfer its energy to the latter, raising the atom to a higher stationary state, the return from the higher energy state being accompanied by the emission of radiation according to Bohr's relation $\nu = \frac{\Delta W}{h}$.

Collisions of this type, in which the translational energy of the particles is totally or partially converted into energy of excitation, are called *collisions of the first kind*. Klein and Rosseland,* however, showed by an argument, based on thermodynamics, that

* *Zeits. f. Physik*, 1921, Vol. 4, p. 46.

the converse process should also be possible and that if a collision occurred between an excited atom and another particle the excited atom might return to its normal state *without emitting radiation*. The energy which ordinarily would appear as radiation, when the atom passed spontaneously from the higher to the lower state, would in this case be expended in increasing the kinetic energy of the colliding particles. A collision in which this occurs is termed a *collision of the second kind*.

The necessity for collisions of the second kind can be realised from the following simple argument. Imagine a collection of atoms, electrons and radiation in a perfectly reflecting enclosure maintained at constant temperature. If it were assumed that the electrons could only be concerned in collisions of the first kind, we should have a mechanism whereby the electrons continually lose energy without being able to acquire it. The electrons would therefore fall in temperature, whereas for the atoms and the radiation the temperature would rise, until finally the energy of the electrons had decreased to a value corresponding to the lowest resonance potential. The setting up of a temperature difference in this way would violate the second law of thermodynamics. It follows that collisions of the second kind must occur.

Franck later extended the same idea to collisions between atom and atom, so that in a collision of the second kind between an unexcited and an excited atom the latter might return to the normal state without radiating, the energy liberated appearing as kinetic energy of translation distributed between the two atoms in accordance with the law of conservation of momentum.*

It has actually been possible to demonstrate experimentally the *transfer of energy of excitation* from an atom of one substance to an atom of another, the transfer definitely taking place in a collision. This phenomenon, in which light from atoms of one kind is re-emitted by atoms of a different kind, was first observed in 1922 by Franck and Cario for a mixture of mercury and thallium vapours. The two metals were placed in separate branches of a

* In the case of molecules, the energy might appear as rotational or vibrational energy. This would lead us to the consideration of the theory of molecular band spectra, a subject we have not discussed.

tube, the mercury being distilled at 100°C ., the thallium at 800°C . The mixture was irradiated with light of wave-length $\lambda\ 2536\cdot7$ from a mercury vapour lamp. Cario obtained with thallium the lines $\lambda\ 5,351, 3,776, 3,520, 3,519, 3,230, 2,918$, all of wave-length greater than $2536\cdot7$, and also the line $\lambda\ 2,238$, which requires a higher excitation energy. The extra energy was provided by the translational energy of an excited mercury atom, in a collision of the second kind. This explanation was confirmed by experiments with cadmium vapour, also excited by mercury. Certain lines, originating from states higher than those corresponding to $\lambda\ 2,536\cdot7$, appeared at high temperatures and not at low temperatures, in quantitative agreement with theoretical prediction.

Similar experiments were made with the mixtures Hg—Pb, Hg—Bi and Hg—Zn.

Bearing in mind these considerations, we recall that in the kinetic theory the molecules of a pure gas were assumed to be identical one with another. This is not absolutely true. Actually, the variety of possible velocities of the molecules in a gas is such that by successive collisions the kinetic energy may be sufficient to bring about the ionisation of the molecule, that is, an electron may be given up. New individuals, electrons and positive ions, then appear in the gas. The electrons can, as already noted, join up with neutral molecules, forming negative ions. Finally, Aston's mass spectra reveal the existence in a gas, of complex molecules (for example, in neon, which is monatomic with atomic weights 20 and 22, molecules of mass 40 were detected).

The simple image of a gas as an assembly of molecules of one kind ceases to be valid, and we are obliged to recognise the presence in a chemically pure gas of electrons, atoms, ordinary molecules, associated molecules, positive and negative ions, and metastable atoms. The gas becomes an extremely complex mixture of particles in perpetual transformation, colliding one with another elastically, inelastically and in collisions of the second kind.

The complexity is alarming, but fortunately without effect on

the fundamental conclusions of the kinetic theory, the distribution of velocities and the equipartition of energy. Every particle, large or small, still possesses on the average the same kinetic energy.

Although a real, chemically pure, gas is always a complicated mixture; there does exist a gas which corresponds to the old conception of the kinetic theory. This is the *electron gas*, which fills the evacuated bulb of a thermionic valve when the filament is heated to incandescence. Electrons evaporate from the filament to form an absolutely homogeneous atmosphere of particles—the *perfect gas*.

Determination of the X-ray Energy Levels

At the present time the production of the various X-ray lines is much more clearly and completely understood than the analogous problem for visible and ultra-violet radiation. The reason is that the visible and ultra-violet lines are produced by changes in the outermost electron shell which is, in general, incomplete and differently constituted in the different atoms. X-rays, on the other hand, originate in transitions between electron shells near the nucleus of the atom. These shells occur in all elements of not too low atomic number, and have the same structure. It is precisely on account of this that the X-ray spectrum is similar for all elements in so far as they give the various X-ray lines.

As we know, the different shells surrounding the nucleus are denoted by the letters K, L, M, N, O, P, Q. The lines of a given group (L for example) are formed by the transition of an electron from one of a number of levels, to a particular level. It is important to remember that whilst the K level has only one energy value, the L level is a triplet, M a quintet and N a septet (see p. 138). What is termed the classification of X-ray lines consists in the precise assignment of two energy levels between which the electron transition occurs which produces the radiation in question.

Bohr's formula $\nu = \frac{\Delta W}{h}$ determines the frequency of the

radiation emitted in the passage of an electron from one level to another with an energy difference of amount ΔW . As the frequencies are known, a large number of *energy differences* are available as material for determining the energy levels themselves. This is the *spectroscopic method*.

When X-rays are excited by the impact of electrons forming the cathode ray stream, the kinetic energy of the electrons $\frac{mv^2}{2}$ is known to equal Ve where V is the voltage applied to the discharge tube. By measuring V the kinetic energy of the electrons, and hence the energy level concerned, can be determined. This procedure is mainly of theoretical interest, for in practice the exact measurement of the voltage V presents great difficulty.

However, we give below a series of values of the voltage V in *kilovolts*, necessary to excite the K series of various elements :

92 Uranium	.	.	.	$V = 115$ Kilovolts.
80 Mercury	.	.	.	82.9
50 Tin	.	.	.	29.1
30 Zinc	.	.	.	9.75
11 Sodium	.	.	.	1.07

It will at once be observed that these potentials are of a much higher order of magnitude than those required to excite the emission of lines in the visible spectrum. The values also show how rapidly the energy of a given level diminishes in passing from heavy to light atoms. The explanation of this variation, which is due to the decrease in the nuclear charge, is obvious. A similar explanation shows why the excitation of other levels, L, M, N, etc., requires much less energy.

The connection between V and the wave-length λ of the most penetrating radiation emitted, is given in practice in the following

form. Since $eV = h\nu = \frac{hc}{\lambda}$, substituting for h its value 6.55×10^{-27} ,

and for the velocity of light c and the electronic charge e , their respective values, we obtain *Duane and Hunt's equation* :

$V\lambda = 12430$; where V is expressed in volts and λ in Ångström units.

In practice λ is known, and is the wave-length corresponding to the highest frequency stimulated in the given element by the voltage V . The numbers given above were obtained by applying the Duane and Hunt formula.

Another important method of finding energy levels makes use of X-ray absorption spectra. When "white" X-rays (X-radiation containing all frequencies) are passed through a thin sheet of a substance, a continuous absorption band is obtained whose long wave edge marks the absorption discontinuity or the point where an emission series is excited. On the photograph of the spectrum the edge of the absorption band can be exactly determined, and thence λ , V , and finally the energy level, are derived. In Chap. V, dealing with the photoelectric effect, another very ingenious method for the exact determination of energy levels will be examined.

The question of the fine structure of X-ray spectra is discussed in Chap. III, p. 137.

*Permanence of the Atoms in Quantum States †

It has frequently been pointed out that if an electron in an atom is displaced from its usual position to a higher quantum state, the atom will return to the normal condition with emission of energy, but up to now nothing has been said of the time during which the electron will remain in the higher quantum state, that is the life period of the excited atom.

This was the subject of extensive researches by Wien, Dempster, and others.

The particles composing the positive rays (Kanal-strahlen) give rise to a complex spectrum, comprising lines emitted by neutral atoms "at rest," ionised atoms at rest, and atoms in motion. On account of the Doppler effect, the latter lines appear displaced in the spectrum relatively to those emitted by atoms at rest. Thanks to this effect it is possible to study the emission of atoms in motion. (Naturally all the atoms are endowed with an average velocity of thermal agitation. Under ordinary conditions this velocity is of the order 10^4 cm./sec. The velocity of canal rays is much greater. Thus for hydrogen, with a tube voltage of 30 KV, $v = 8.85 \times 10^7$ cm./sec. It is permissible therefore to neglect the velocity of thermal motion.)

W. Wien in the years 1919 to 1925, and later A. J. Dempster (1920 to 1923), devised experiments which allow us to study the emission of atoms undisturbed by collisions with other atoms. In principle, the method is analogous to that adopted by J. J. Thomson (see Vol. I, Chap V) and by Aston. The canal rays produced in a discharge tube A pass into another compartment B. By the aid of powerful pumps which in general are kept running throughout the whole time of the experiment, the pressure in B is maintained at so low a value that

† Bibliography. W. Wien, *Ann. d. Phys.*, 1919, 1921, 1923, 1924, 1925. A. J. Dempster, *Phys. Rev.*, 1920; *Astrophys. Journ.*, 1923. E. A. Milne, *Monthly Notices*, 1924. B. Dasannocharya, *Ann. der Physik*, 1929.

The coefficient of proportionality A_m^n is a constant characteristic of the atom and of the emission frequency corresponding to the transition $n - m$. For a large number N_n of atoms in the quantum state n , the number passing to the state m in unit time is clearly given by,

$$\frac{dN_n}{dt} = - N_n A_m^n \dots \dots \dots (4)$$

dN_n equals the number of atoms emitting light in the time dt .

Multiplying both sides of the above equation by $h\nu$, we obtain an expression for the energy emitted by the N_n atoms per unit time :

$$\frac{dE}{dt} = - N_n A_m^n h\nu \dots \dots \dots (5)$$

Integration of (4) gives :

$$\begin{aligned} \frac{dN_n}{N_n} &= - A_m^n dt \\ \log N_n &= - A_m^n t + \text{constant} \\ N_n &= K e^{-A_m^n t} \dots \dots \dots (6) \end{aligned}$$

Thus N_n decreases exponentially with time, and it follows from (5) that the rate of emission of radiation diminishes according to the same law. This result is in complete agreement with the experimental law (2) found by Wien. If a group of N_n atoms forming the canal ray stream, all in the quantum state n , moves with constant velocity v in the tube B, then as the distance covered vt increases, the number of excited atoms will decrease according to the formula (6). The luminous intensity which is proportional to $\frac{dN_n}{dt}$ will diminish with increase of x in analogous fashion.

To sum up, the classical and quantum theories lead to the same final formulæ, and it is only in the interpretation of the constants that they differ.

$\tau = \frac{1}{\gamma}$ in one case represents the "time of emission" or the time of damping of the vibrations. In the quantum theory, on the other hand, $\tau = \frac{1}{A_m^n}$ measures

the average duration of the quantum state n (when the only possible transition is n to m). It seems that a crucial experiment to decide between these two interpretations cannot be obtained.*

We shall now show that by applying the correspondence principle according to which for high quantum numbers the quantum theory results must reduce to those of classical electrodynamics, it is possible to calculate the order of magnitude of the average duration of the quantum states for the hydrogen atom.

The classical theory indicates that a particle of charge e subjected to an acceleration a , radiates energy of amount $\frac{2}{3} \frac{e^2}{c^3} a^2$ per unit time. If r is the radius of the circular orbit described by the electron of the hydrogen atom, its acceleration will equal $\frac{e^2}{mr^2}$ and as $r = \frac{h^2 n^2}{4\pi^2 m e^2}$ we have for the rate of emission of radiation,

$$W = \frac{2}{3} \frac{e^2}{c^3} a^2 = \frac{512 \cdot \pi^8 m^2 e^{14}}{3 c^3 h^8 n^8}$$

* Quantum mechanics reconciles the two points of view in a way which cannot be explained here.

Denoting by τ the time during which this emission is maintained, the total quantity of energy radiated W_τ should be the same as that furnished by the quantum theory, for a transition from the orbit of quantum number n to the neighbouring orbit of quantum number $n - 1$. The energy emitted in the latter process is known to equal,

$$\frac{2\pi^2me^4}{h^2} \left\{ \frac{1}{(n-1)^2} - \frac{1}{n^2} \right\}$$

and equating this expression to W_τ we obtain :

$$\frac{512 \cdot \pi^8 m^2 e^{14}}{3c^3 h^8 n^8} \tau = \frac{2\pi^2 me^4}{h^2} \left\{ \frac{1}{(n-1)^2} - \frac{1}{n^2} \right\}.$$

Using this result, the following formula for the *average life* τ is easily arrived at :

$$\tau = 4.5 \times 10^{-11} n^6 \frac{2n-1}{(n-1)^2}$$

For hydrogen, in the transition to the normal state n must be put equal to 2, and we obtain $\tau = 0.8 \times 10^{-8}$ sec.

*Spectra of Molecules

The subject of molecular spectra is very important and, at the same time, very complicated. We shall be obliged to limit our discussion to giving some idea of the theoretical aspect. Molecules give rise to so-called *band* spectra. This name was introduced at a time when only spectrosopes of low resolving power were available. The component lines of the bands were indistinguishable individually and appeared merged together into a strip of graded intensity. The fact that spectra of this character are actually due to molecules is established by the disappearance of the bands when the emitting gas is heated to temperatures at which the molecules dissociate into atoms.

Band spectra are of two kinds. Those in the visible and ultra-violet region consist of closely packed groups of lines converging onto the so-called *head of the band*. The spectrum usually contains several such bands, each with the head turned towards the red or towards the violet. The second type consists of the infra-red bands which are formed of groups of lines separated by constant frequency differences.

As in the case of atoms, these spectra result from the existence of different energy levels of the molecule. We consider, for simplicity, only diatomic molecules (hydrochloric acid, hydrobromic acid, cyanogen, etc.). The energy of a molecule

is made up of the energy (W_e) of electron motion with respect to the nuclei regarded as fixed, energy associated with an oscillatory motion of the nuclei and energy of rotation of the nuclei about an axis at right angles to their joining line.* We consider the separate quantisation of these motions. The oscillation gives, we know, the series of stationary states :

$$W_2 = nh\nu_0 \quad \text{with } n = 0, 1, 2, 3, 4, \dots$$

The rotation, on the other hand, gives rise to the series :

$$W_3 = \frac{h^2 m^2}{8\pi^2 I} \quad \text{with } m = 0, 1, 2, 3, 4, \dots \dagger$$

The total energy of the molecule (except for an additive constant) is then :

$$W = W_e + nh\nu_0 + \frac{h^2 m^2}{8\pi^2 I}$$

We now apply Bohr's rule to obtain the frequencies of the lines to which the molecule can give rise by transitions between stationary states. The variation of the total energy, ΔE , will be accompanied by the emission of the frequency $\nu = \frac{\Delta E}{h}$:

$$\nu = \frac{W'_e - W_e}{h} + (n'\nu_0' - n\nu_0) + \frac{hm'^2}{8\pi^2 I'} - \frac{hm^2}{8\pi^2 I}$$

The whole system of the possible emission frequencies is

* Of course, the mutual energy of the electrons and the intrinsic energies of the nuclei also come in. Ordinarily, however, these contributions have little influence on the spectrum of the molecule. Actually there are molecules, such as H_2 , for which the effect of the magnetic moments of the nuclei becomes the dominating factor.

† The energy of rotational motion is $W = \frac{1}{2}I\dot{\phi}^2$ (ϕ = angle of rotation, I = moment of inertia). Remembering that $p = \frac{dW}{d\dot{\phi}} = I\dot{\phi}$, Sommerfeld's

condition $\int_0^{2\pi} p d\phi = mh$ becomes $\int_0^{2\pi} p d\phi = I\dot{\phi} \int_0^{2\pi} d\phi = 2\pi I\dot{\phi} = mh$.

Hence $m^2 h^2 = 4\pi^2 I^2 \frac{2W}{I}$.

The energy is therefore quantised, $W = \frac{h^2 m^2}{8\pi^2 I}$, or in other words* is capable of assuming only the discrete series of values obtained by putting $m = 0, 1, 2, \dots$ etc.

contained in this formula, subject to the restriction $m' = \begin{cases} m \pm 1 \\ m \end{cases}$ imposed by the selection rule.

The electronic terms W'_e , W_e may be equal or they may be different, and as they are generally of a higher order of magnitude than the terms $n\nu_0$, $n'\nu_0'$, in the former case the frequency lies in the infra-red and, in the latter case, in the visible or ultra-violet.

When W_e is different from W'_e (visible and ultra-violet bands) there are three bands: the first corresponding to all values n , n' with $m' = m + 1$, the second corresponding to all values n , n' with $m' = m$ and the third with $m' = m - 1$. The infra-red bands on the other hand occur for $W'_e = W_e$. It should be noted that as the frequency ν_0 and the moment of inertia depend only on the electronic energy, in this case,

$$\nu_0 = \nu_0' \text{ and } I = I'$$

Hence,

$$\nu = \nu_0(n' - n) + \frac{h}{8\pi^2 I} (1 \pm 2m),$$

where allowance has been made for the selection rule which requires $m' - m = \pm 1$.

If $n' - n$ is kept fixed and m is varied, a series of lines is obtained, separated by a constant frequency interval of amount,

$$\Delta\nu = \frac{h}{4\pi^2 I},$$

and it is in fact this succession of lines which constitutes an infra-red band. The above expression for $\Delta\nu$ is important, as from it the moment of inertia of a molecule can be calculated.

For example, the molecule of hydrogen chloride emits infra-red bands in which the frequency difference between consecutive lines equals $\Delta\nu = 6.3 \times 10^{11}$. Using this value to calculate $I = 2.6 \times 10^{-40}$, it is easy to determine *the distance d separating the hydrogen and the chlorine nuclei*. Making the calculation,* d comes out to be $d = 1.27 \times 10^{-8}$ cm.

* The moment of inertia $I = \frac{m_1 \times m_2}{m_1 + m_2} d^2$, where m_1 and m_2 represent the masses of the chlorine and hydrogen nuclei. $m_1 = 59 \times 10^{-24}$ gm. $m_2 = 1.66 \times 10^{-24}$ gm. Hence $I = 1.61 \times 10^{-40} d^2$.

The spectra of molecules were studied in particular by Deslandres (1887), later by Bjerrum (1912) and Rubens, and then by Schwarzschild, Imes, Heurlinger, Lenz, Kratzer, etc.

It is of interest to note that if a molecule of HCl contains, instead of the chlorine atom of atomic weight 35, the atom of the chlorine isotope of atomic weight 37, the moment of inertia I will be slightly different, and as a result the frequency of any given line will be altered. In this way a fine structure of molecular spectra, due to the existence of isotopes, makes its appearance. The effect has been actually observed with the spectroscope, and from the width of the doublet it was possible to work back to the change in moment of inertia and, finally, to the difference in mass of the isotopes. The results agreed perfectly with Aston's values determined from measurements with the mass spectrograph.

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CHAPTER III

STARK AND ZEEMAN EFFECTS. MULTIPLET LINES. THE SPINNING ELECTRON

IN discussing the hydrogen atom, very little has been said of the applications of Bohr's theory and of Sommerfeld's further developments of the theory. This course was adopted to avoid obscuring the reader's vision of the whole theory by immersing him in a mass of detail. In the present chapter, the developments mentioned will be examined in greater detail, although again it will be necessary to omit the long and complicated calculations which underlie the results.

A complete treatment of the dynamical problem of the electrons of the atom has been effected only in the case of the hydrogen atom, where there are involved no more than two masses. Here we have to deal with the astronomical problem of the motion of a planet about a sun, whose mass—compared with that of the planet—is so great that the sun can be regarded as stationary. This is obviously the simplest conceivable problem. If, however, the mass of the sun is not infinite compared with that of the planet, the problem immediately becomes a little more complicated, and this is so in the actual case of hydrogen. If the rotating mass has a very high velocity, of the order of the velocity of light, relativity enters and the problem undergoes a further complication. In this form the problem corresponds precisely with the case of the hydrogen atom in which the electron moves with a very high velocity, although the relativity effect is small and in certain connections can be neglected to a first approximation, in discussing the spectrum.

If the atom is situated in an electric or magnetic field the electron describes orbits which are not elliptical, and we have the problems of the Stark and the Zeeman effects.

The above constitute the group of problems associated with the hydrogen atom. These and other more complicated problems have been treated by the methods of quantum mechanics, as we shall see in Chap. VIII, and it has been established (1925) that the latter and not classical mechanics, hold good for atomic phenomena. Thus the remarkable successes of the mathematical physicists outlined in the present chapter were to a certain degree the result of chance.

Elliptical Orbits. Sommerfeld's Theory

We have seen that Bohr, in his discussion of the problem of the hydrogen atom, considered circular orbits; but in the general case of the motion of a mass point under the action of a coulombian central force

$$\left(F = \frac{Q}{r^2}\right), \text{ the orbit}$$

described is an ellipse, one focus of which is occupied by the attracting mass. Sommerfeld, therefore, also considering the simplest case, the hydrogen atom, set himself to study the elliptical orbits. Now,

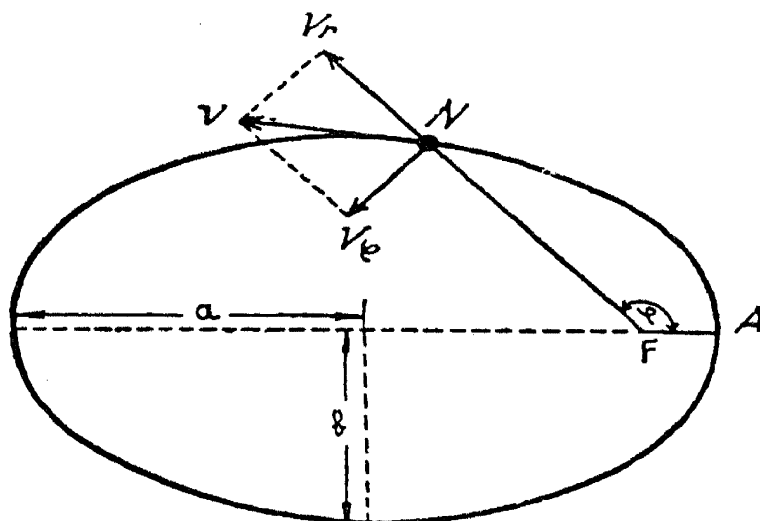


FIG. 20

whilst a circle is defined by a single parameter, the radius, an ellipse is specified by two parameters, for example, the two semi-axes. Thus in the same way as in Bohr's theory by fixing the quantum number the orbit is completely determined, so—as we shall see immediately—*two* integral quantum numbers define the elliptical orbit and hence the *energy of the stationary state*.

Let m be the mass of the electron, e its charge, and Ze the charge of the attracting centre (see Fig. 20). To quantise the motion, in other words, to determine all the privileged ellipses in one plane, Sommerfeld lays down the analytical conditions :

$$\oint p_{\phi} d\phi = n_1 h \quad \int p_r dr = n_2 h,$$

h is Planck's constant. p_ϕ and p_r are the "momentum variables" corresponding to the "positional variables," ϕ , the azimuthal angle, and r , the radius vector. The momentum variables as in Newtonian mechanics as elaborated by Hamilton and Poisson and are defined by the relations :

$$p_\phi = \frac{\partial T}{\partial \dot{\phi}} \quad p_r = \frac{\partial T}{\partial \dot{r}},$$

where T is the kinetic energy of the system. Sommerfeld's integrals are extended over a closed curve, *i.e.*, they cover variations of r and ϕ in a complete cycle of the system, which explains the adoption of the symbol \oint . Without entering analytical details, we proceed at once to the result arrived at by Sommerfeld.

It is found that,

$$E_{\text{total}} = -\frac{Ze \cdot e}{2a} = -\frac{Rh}{(n_1 + n_2)^2} \left(\frac{Ze}{e}\right)^2$$

$$p_\phi = a m e \cdot Ze(1 - \epsilon^2)$$

$$a = (n_1 + n_2)^2 h^2 / (4\pi^2 m e \cdot Ze.)$$

where $R = \frac{2\pi^2 m e^4}{h^3}$, ϵ = the eccentricity and a the major semi-axis of the ellipse.

Thus all motions for which the total quantum number $n_1 + n_2$ has the same value, correspond to the same major axis and same energy. On the other hand, the distribution of the quantum number between radial quantum number n_2 and azimuthal quantum n_1 , fixes the eccentricity of the ellipse as given by :

$$1 - \epsilon^2 = \frac{n_1^2}{(n_1 + n_2)^2}, \quad \epsilon = \text{eccentricity.}$$

Fixing a value for the sum $n_1 + n_2$, we obtain a number of ellipses of different eccentricities, but all having the same major axis, as already explained in the previous chapter. Knowing the energy corresponding to the various preferred orbits, we can apply Bohr's second postulate. When the electron passes from one

orbit to another there occurs emission or absorption of radiation of frequency ν given by the relation,

$$\nu = \frac{E_1 - E_2}{h}.$$

Hence *all* the possible frequencies are contained in the general formula,

$$\nu = R \left(\frac{Ze}{e} \right)^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where n_1, n_2 are now the *total* quantum numbers corresponding respectively to the two orbits concerned.

For hydrogen the charge of the nucleus and that of the electron are equal, $Ze = e$, and we obtain once more the familiar formula,

$$\nu = R \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right), \text{ with } R = \frac{2\pi^2 m e^4}{h^3}.$$

A detailed discussion of this formula has already been given in Chap. II.

***Stark-Lo Surdo Effect. Trajectories of the Electron of the Hydrogen Atom in an Electric Field**

We know that the spectrum of hydrogen in an intense electric field is much more complicated than under ordinary conditions. This is the Stark-Lo Surdo effect.

The experimental results of Stark and Lo Surdo are of several kinds. Each line of the Balmer series is split up into a certain number of components, the number increasing with the ordinal number of the series. These components are polarised in a particular way, details of which for the sake of simplicity we pass over for the moment. The components separate out symmetrically on either side of the original line. The distances of the components from the centre of the system are integral multiples of the distance from the centre, of the least displaced component, and the latter distance increases in proportion to the strength of the field. The problem is to give a complete explanation of these experimental observations.

The search for a possible resolution of spectral lines by an

electric field naturally suggested itself, after Zeeman's discovery (1896), of the effect of a magnetic field. It was, however, not until 1913 that Stark succeeded for the first time in demonstrating such a phenomenon. The difficulty was the production of a powerful electric field within a gas emitting light, gas in that condition being a good conductor and incapable of sustaining a field. This difficulty was overcome at about the same time by Stark in Germany and Lo Surdo in Italy, using different methods.

Stark's apparatus is shown in Fig. 21. AA is the anode ; close behind the perforated cathode CC is placed the plate FF. Between

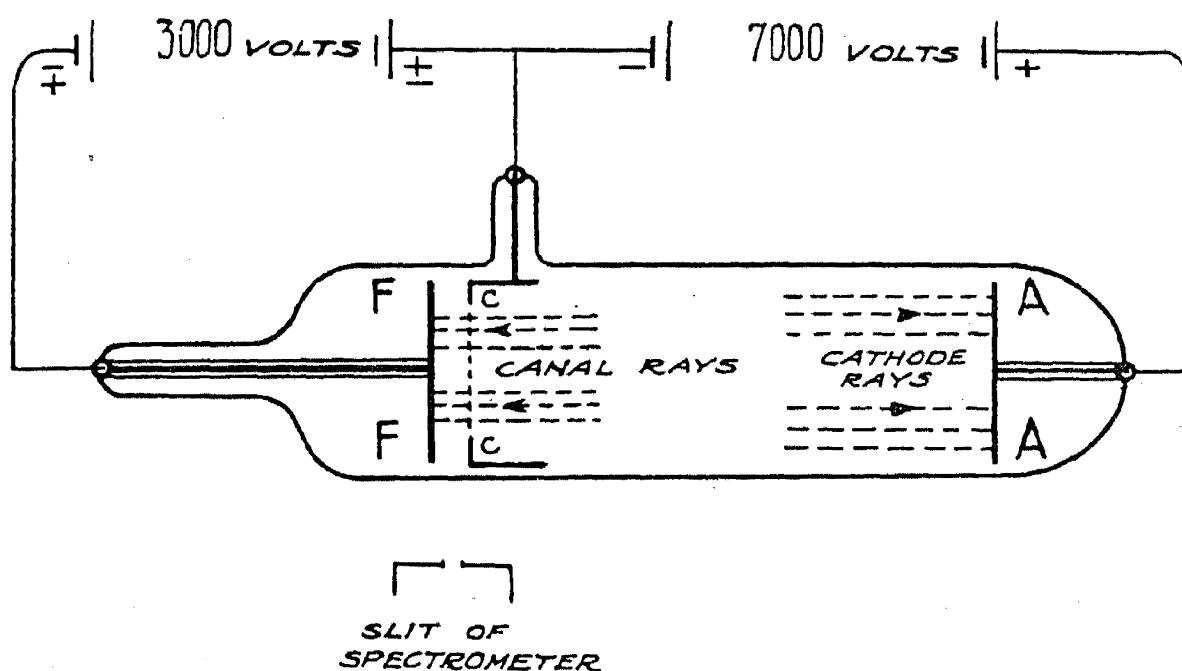


FIG. 21.—Stark's Experimental Arrangement.

AA and CC is applied the field generating the canal rays which pass through the apertures in CC, and between FF and CC the field producing the effect, which is observed by means of a spectroscope. The spectroscope reveals the separation of the lines.

The distance between FF and CC is only 2 to 3 mm. and the pressure in the tube is so low that the mean free path of the ions greatly exceeds this distance. Thus, in the space under observation no production of secondary ions by collision occurs and there is no gas discharge.

Lo Surdo's apparatus consisted of a hydrogen tube with the part close to the cathode constructed in the form of a narrow

act which had the effect of producing a rapid fall of
It was just in this part of the tube that the effect was

discuss the Stark-Lo Surdo effect in the case of
aly.

ars after the discovery of the Stark-Lo Surdo effect,
t mathematical physicists, Schwarzschild and Epstein,*
mathematical solution of the problem, based on the
theory which Bohr had propounded several years earlier,
out the same time as the discovery of the effect in

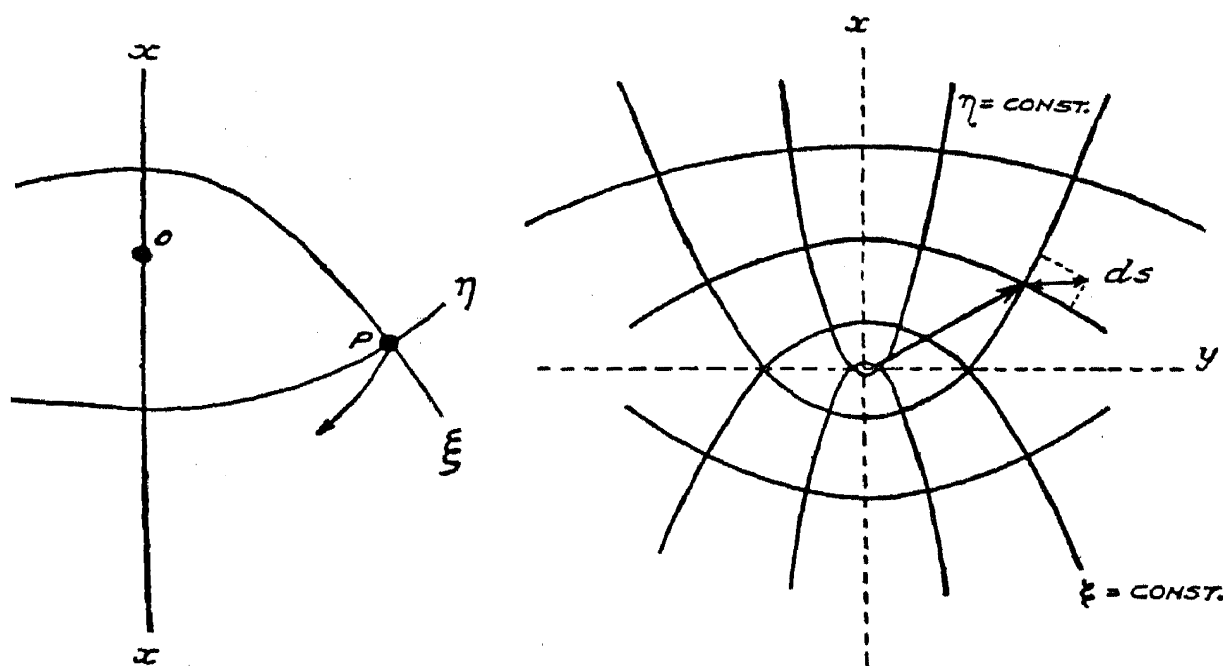


FIG. 22.

The explanation in detail of all the features of the
et was in fact one of the most astonishing successes of
im theory. We shall limit ourselves to giving some idea
ne problem is resolved, the complete solution being
laborious.

t step is to find the trajectories of an electron subjected
ion of a uniform electric field of intensity F in addition
d of the nuclear charge Ze ($Z = 1$ for hydrogen). As
ld points out in his classical treatise, this problem is a

Theorie des Starkeffektes," Epstein, *Ann. d. Physik*, 50, 1916.
schild, *Berlin Berich.*, p. 548, 1916.

special case of the more general problem in which a point moves under the influence of two coulombian attractions. For the uniform field, one attracting centre is removed to infinity. The most convenient co-ordinates to work with in the present case are the parabolic co-ordinates used in astronomy, as when this is done the Jacobi equations are obtained in separable form.

The position of a point P *in a plane* can be defined as the intersection of two confocal parabolæ, with their foci at the attracting centre and having a common axis parallel to the direction of the field F. Passing from the plane to three dimensional space, the complete figure is rotated about the axis xx (see Fig. 22). In this way any point of space is determined as the intersection of two parabolæ specified by the parameters ξ and η and by the angle ψ , giving the amount of rotation of the whole figure with respect to a fixed plane. Hence the electron position is defined by the three values ξ, η, ψ . The two co-ordinates ξ, η , are related to the cartesian co-ordinates by the formulæ :

$$x = \frac{1}{2}(\xi^2 - \eta^2) \quad y = \xi\eta \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which express the fact that if η is constant, the points defined by different values of ξ lie on a parabola of axis xx .* It is now clear what is meant by the statement that η is the parameter of the parabola.

The problem now is to obtain Jacobi's equation representing the motion of the system. The kinetic energy is $E_{\text{kin}} = \frac{m}{2} \left(\frac{ds}{dt} \right)^2$, and it is easy to express the element of arc ds as a function of the differentials $d\xi, d\eta, d\psi$ of the three co-ordinates (see second diagram of Fig. 22). The potential energy clearly has the value $E_{\text{pot}} = \frac{Ze^2}{r} + eF\bar{x}$, which is the sum of the coulombian term $\frac{Ze^2}{r}$ and the term $eF\bar{x}$ representing the work done by the field F.

The function $E_{\text{kin}} + E_{\text{pot}}$ is the Hamiltonian function, and, as we know, it remains invariant during the motion, representing the

* Eliminating ξ from (1) gives $\frac{y^2}{\eta^2} - 2x = \eta^2$ which for $\eta = \text{constant}$ is the equation of a parabola having xx for axis.

total energy of the system. We write $E = E_{\text{kin}} + E_{\text{pot}}$ for the total energy and introduce the "momentum," variables,

$$p_{\xi} = \frac{\partial S}{\partial \xi} = \frac{\partial E_{\text{kin}}}{\partial \xi'}, \quad p_{\eta} = \frac{\partial E_{\text{kin}}}{\partial \eta'}, \quad p_{\psi} = \frac{\partial E_{\text{kin}}}{\partial \psi'}.*$$

Making a number of simple transformations we obtain Jacobi's partial differential equation :

$$\begin{aligned} \left(\frac{\partial S}{\partial \xi}\right)^2 + \left(\frac{\partial S}{\partial \eta}\right)^2 + \left(\frac{1}{\xi^2} + \frac{1}{\eta^2}\right) \left(\frac{\partial S}{\partial \psi}\right)^2 \\ = 2m(\xi^2 + \eta^2)E + 4me^2Z - meF(\xi^4 - \eta^4). \end{aligned}$$

In this equation the three variables are separable and the complete solution of the problem can therefore be obtained.

We pass at once to the final result. Having laid down the three Sommerfeld conditions :

$$\int p_{\xi} d\xi = n_1 h \quad \int p_{\eta} d\eta = n_2 h \quad \int p_{\psi} d\psi = n_3 h$$

it is possible as usual to express the total energy E in terms of the quantum numbers, and for a rather weak field F (F^2 negligible compared with F) the final formula runs,

$$E = -\frac{2\pi^2 me^4 Z^2}{(n_1 + n_2 + n_3)^2 h^2} - \frac{3}{8} \frac{h^2 F}{\pi^2 me Z} (n_2 - n_1)(n_1 + n_2 + n_3)$$

This result may be written in a simpler form remembering that in the absence of field ($F = 0$), E reduces to the first term only :

$$\text{Epstein's formula} \quad \Delta E = \frac{3}{8} \frac{h^2 F}{\pi^2 me Z} (n_2 - n_1)n.$$

It is clear that in the passage of an electron from an orbit of *total quantum number* n to another orbit of *total quantum number* s , we no longer obtain a single line as in the case of zero external electric field, but several lines. The difference of frequency between the lines corresponding to transitions to orbits of quantum numbers s_1, s_2, s_3 and s_1^1, s_2^1, s_3^1 respectively ($s_1 + s_2 + s_3 = s = s_1^1 + s_2^1 + s_3^1$), is given by

$$\Delta \nu = \frac{\Delta E - \Delta E^1}{h} = \frac{3Fh}{8\pi^2 me Z} [(s_2 - s_1)s - (s_2^1 - s_1^1)s].$$

* S is the *action* which is defined by the equation $\int 2E_{\text{kin}} dt = S$.

In the passage from the orbit n to the orbit s emission of a single line took place in the absence of the electric field. The field, however, has deformed in different ways the orbits with the same value of the sum of the three quantum numbers, and as a result these now have different energies. The lines which before were all exactly superimposed owing to the fact that the energy depended solely on the sum of the quantum numbers, now separate. The decomposition is symmetrical about the original line and increases in complexity with the total quantum number. The

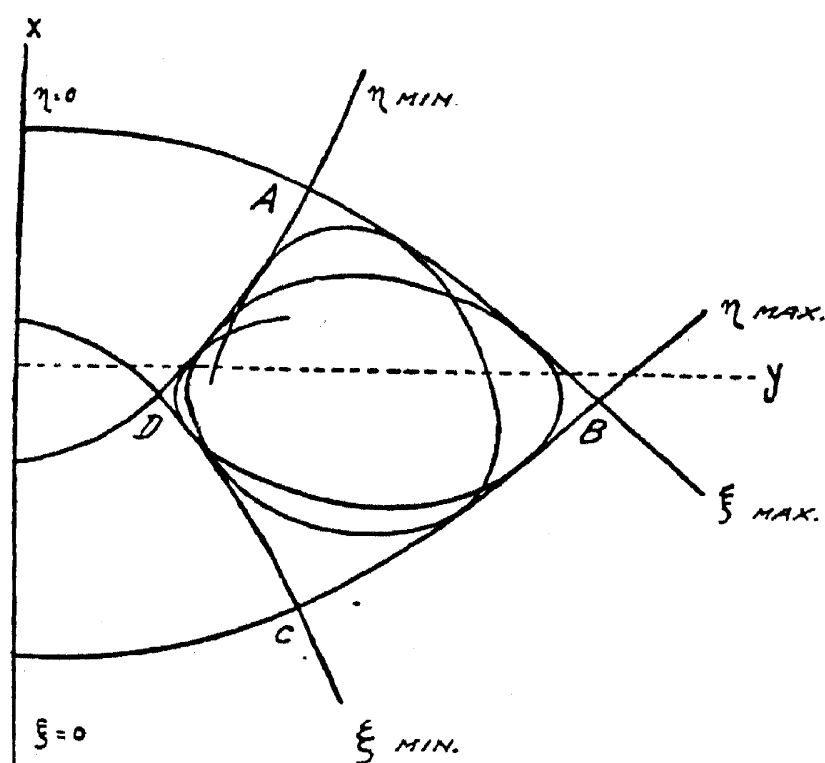


FIG. 23.

amount of separation increases in proportion to the field strength. As the minimum value of the term in square brackets is unity, and all the other values are integers, the formula explains the fact that the displacement of lines originating from a given line, are integral multiples of a certain minimum distance.

Without going into lengthy details here, we may say that all the varied and complex features of the Stark effect are exactly predicted by the theory sketched above.

What of the orbits described by the electron? The co-ordinate η varies between a minimum value η_{\min} and a maximum value

ξ also oscillates continually between ξ_{\min} and ξ_{\max} . It is that all the trajectories are contained in the toroidal region bounded out by the curvilinear quadrilateral A, B, C, D (see Fig. 1).

The electron passes from a tangential contact with a parabola of the η group to a tangential contact with a parabola of the μ group, and, meanwhile, it has also to rotate about the axis of the electric field.

The position of the electron in projection on the axis xx' is constant whose distance from the attracting centre measures the *electrical polarisation* of the atom under the influence of the electric field E .

Regarding the periodicities of the oscillations in the three variables, these differ one from another (as is always the case in conditionally periodic motions). In the absence of the electric field, the electron describes a closed ellipse so that the two periods relative to the two co-ordinates (azimuthal angle and radial distance) are equal, but on introducing the electric field three periods are generated.

The effect of an electric field on the spectrum of hydrogen is quite different from the effects observed in the spectra of other elements which we have not space to discuss here.

Zeeman Effect

In 1896 Professor Zeeman, of Amsterdam, discovered that spectral lines are influenced by a magnetic field. He showed that spectral lines emitted by a luminous vapour in a magnetic field split up into a number of components whose distance apart increases with the intensity of the magnetic field.

In the simplest case, when the light beam analysed by the spectroscope is parallel to the magnetic field, a doubling of the lines is observed. When the beam is perpendicular to the field, three lines appear, one of which occupies the position of the original line, the other two being displaced equally on either side of the original line by an amount as the two lines in the longitudinal effect. The displacement, expressed as a frequency shift, is :

$$\Delta\nu = \frac{e}{m_0} \frac{H}{4\pi c} = 4.70 \times 10^{-5} H,$$

H being measured in gauss. The effect is always very small, and to detect it spectrometers of high resolving power are required.

To apply the quantum theory to the explanation of the Zeeman effect, consider the atom of hydrogen composed of a nucleus and one electron. What is the trajectory of the electron in the presence of a magnetic field of intensity H ? The answer to this question is provided by a theorem due to Larmor. We shall omit the proof and pass immediately to an explanation of the result.

The electron describes exactly the same orbits as in the absence

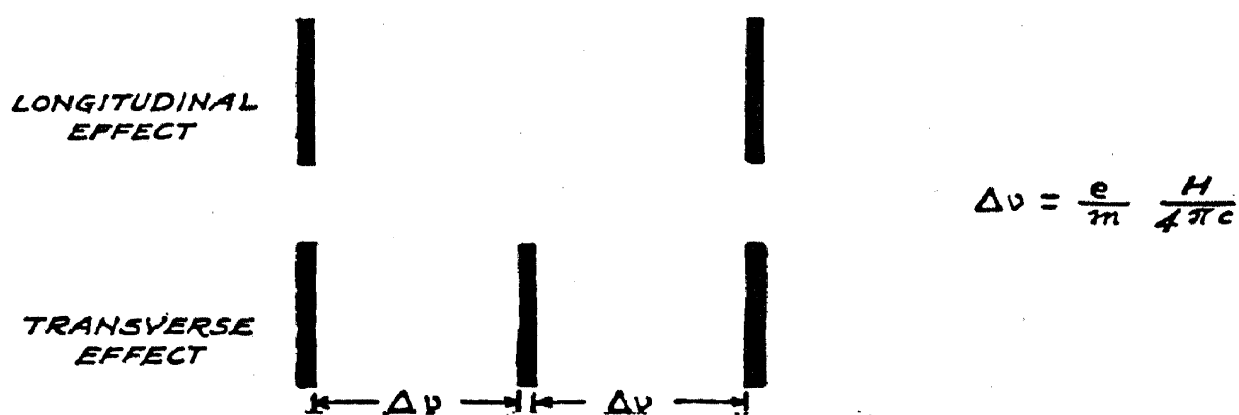


FIG. 24.

of the magnetic field, but relatively to a system of reference which rotates about the field direction with angular velocity :

$$\omega = \frac{1}{2} \frac{e}{m_0} \frac{H}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

m_0 = mass of the electron,

c = velocity of light.

We remark in passing that c enters here because the force exerted by a magnetic field H on a particle of charge e and velocity v , equals in electromagnetic units $\frac{e}{c} [vH]$, where $[vH]$ denotes the vector product of v and H .

Thus the trajectories remain the same, but acquire progressively and slowly the velocity of precession ω , which is always very small compared with the velocity of revolution of the electrons in their orbits (*Larmor precession*.)

To ascertain the total energy, or rather its variation, we must,

as usual, investigate the expressions for the potential and kinetic energy. The former is not changed, as the distance r of the electron from the nucleus does not alter when the magnetic field is applied.

It is easily shown, however, that the kinetic energy, owing to the rotation of the trajectory, varies by the amount :

$$\Delta E_{\text{kin}} = \frac{n\omega h}{2\pi} \quad (2)$$

where n is the quantum number with respect to the axis z , *i.e.*, in the direction of the magnetic field.

This requires further explanation. Let O be the nucleus

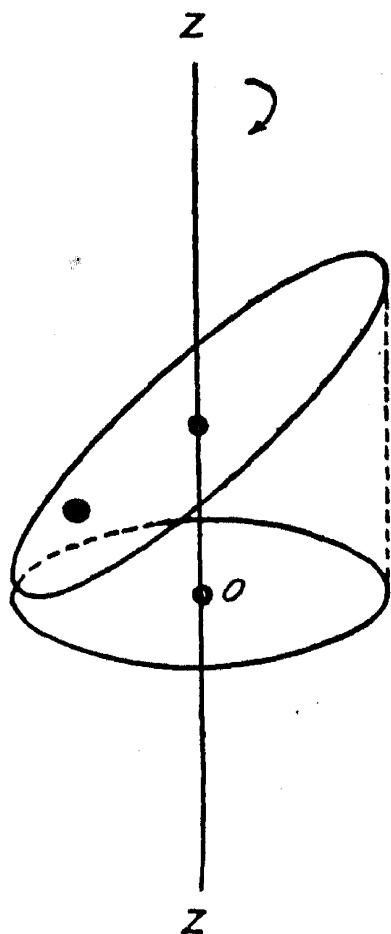


FIG. 25.

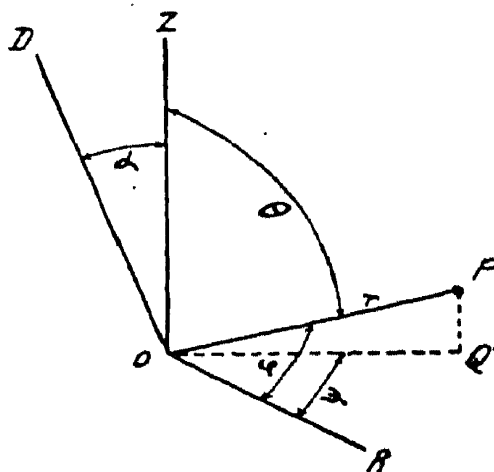


FIG. 26.

(Fig. 26), P the electron, OD the normal to the plane of the elliptical orbit. OR is the intersection of the orbital plane with the plane normal to OZ , and is the origin from which the azimuthal angles ϕ in the plane of the trajectory are measured. If, on the other hand, we consider the motion of the electron in space, its three co-ordinates are the angle θ , the radius vector r , and the

angle ψ measured in the equatorial plane, *i.e.*, the plane normal to OZ, the field direction.

It follows that applying the quantum conditions in the plane of the ecliptic, we shall have,

$$\int p_r dr = n_2 h \quad \int p_\phi d\phi = n_1 h.$$

If the quantisation is effected with respect to the three co-ordinates, the quantum conditions are :

$$\int p_r dr = n_2 h \quad \int p_\psi d\psi = n_3 h \quad \int p_\theta d\theta = n_4 h.$$

Now, we know that $2T = \Sigma p_i \dot{q}_i$ in both reference systems.* Hence,

$$2T = p_r \dot{r} + p_\phi \dot{\phi} = p_r \dot{r} + p_\psi \dot{\psi} + p_\theta \dot{\theta} \quad . \quad . \quad . \quad . \quad (3)$$

which gives the kinetic energy at each instant, in the two systems of co-ordinates. Integrating over a complete revolution :

$$n_2 h + n_1 h = n_2 h + n_3 h + n_4 h.$$

Thus the following relation subsists between the quantum numbers :

$$n_1 = n_3 + n_4.$$

Furthermore, and this is most important,

$$n_3 = n_1 \cos \alpha.^\dagger$$

The angle α is therefore related to the values of the quantum numbers n_1 n_3 .

It follows that *the orbital plane can assume only certain well-defined positions* with respect to the direction of the field. This is what is known as **spatial quantisation**. For example, if the azimuthal quantum number n_1 , has values 1, 2, 3, 4, etc., the following positions are possible (in each case there are, in all, n_1 positions) :

* T is the kinetic energy ; p_i is the momentum variable corresponding to the generalised coordinate q_i .

† Note that p_ψ and p_ϕ are connected by the simple relation : $p_\psi = p_\phi \cos \alpha$, since p_ψ is the moment of momentum about OZ, p_ϕ the moment of momentum about OD, and the former is the projection of the latter. Hence for a complete revolution $2\pi p_\psi = n_3 h = 2\pi p_\phi \cos \alpha = n_1 h \cos \alpha$, from which we deduce $n_3 = n_1 \cos \alpha$.

if $n_1 = n_3 + n_4$ has the value 1 there will be only one possible position, $\cos \alpha = 1$ or $\alpha = 0$ with $n_4 =$ zero.

if $n_1 = 2$, there will be two possible positions since n_3 may be zero or 1, and hence $\cos \alpha = \frac{1}{2}$ or 1.

if $n_1 = 3$, there will be 3 possible positions, $\cos \alpha = \begin{cases} \frac{1}{2} \\ \frac{2}{3} \\ 1 \end{cases}$

and so on.

An important confirmation of this spatial quantisation will be met with in Chap. VII.

Thus we have arrived at this rule which states that in the presence of a magnetic field the orbital plane can assume only a few discrete orientations, and the significance of the quantity n_3 , the quantum number with respect to the axis OZ, has become clear.

We now come to the final step. In the act of transition from one orbit to another, the variation in the energy due to the magnetic field is, from what has been said,

$$\frac{(n_3 - n'_3)h\omega}{2\pi} = (n_3 - n'_3) \frac{eHh}{4\pi m_0 c}$$

and the variation in the frequency, $\Delta\nu$, is obtained by applying the usual Bohr rule $\Delta\nu = \Delta E/h$:

$$\Delta\nu = (n_3 - n'_3) \frac{eH}{4\pi m_0 c}.$$

At this point, use must be made of the *selection rule* which we shall explain briefly on p. 127. According to the selection rule, in the passage of an atom from one configuration to another, the quantum numbers can only vary by an amount $+1$ or -1 or zero. Hence we must have always: $n_3 - n'_3 = +1$ or -1 or 0.

The frequency change in the Zeeman effect, *i.e.*, the displacement of the lines, can therefore only equal zero, $\pm \frac{e}{m_0} \frac{H}{4\pi c}$. To the value $n_3 - n'_3 = 0$ corresponds $\Delta\nu =$ zero. In other words, there is no displacement of the line observed in the spectrum.

This result is in complete agreement with the experimental facts, namely, the formation of doublets, with or without the presence of the original line. It may be mentioned that the theory

also explains the polarisation of the lines, which we cannot stay to consider.

The quantum theory of the Zeeman effect is due to Debye.

We observe that the expression $\Delta\nu = \frac{1}{4\pi c} H \frac{e}{m_0}$ provides another method distinct from those already met with, for determining the ratio $\frac{e}{m_0}$ of the charge to the mass of the electron. Many experimenters, Weiss, Cotton, Fortrat, and others, have made such determinations. In 1923 Babcock, at the Mount Wilson Observatory, obtained the value 1.761×10^7 .

Before leaving the subject, it will be useful to make a few further observations which will be of value in dealing with the anomalous Zeeman effect and which will come up again in Chap. VII when we consider the subject of magnetism.

Imagine an electron moving round in a small circle. Up to now we have always considered the *moment of momentum* vector only, and no reference has been made to the fact that the electron in motion generates a magnetic field, identical in all respects with that of a small magnet of magnetic moment M placed at the centre, and perpendicular to the plane of the electron orbit.

It is easy to show that the magnetic moment M and the moment of momentum P , are related by the equation,

$$M = \frac{eP}{2m_0c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which is also valid when the trajectory of the electron is elliptical. It is a consequence of Kepler's laws that P is a constant during the motion.

We observe now that all the projections of P on the invariable axis of the moments are integral multiples of $\frac{\hbar}{2\pi}$, and hence their vector sum is also a multiple of this quantity. It follows that for a system containing electric charges in motion, the total magnetic

moment will be related to the aggregate moment of momentum again by the law (\perp) above, and that,

$$M = m \frac{eh}{4\pi m_0 c},$$

where m is an integer.

The quantity $\frac{eh}{4\pi m_0 c} = 0.91 \times 10^{-20}$ is a universal constant. It represents the smallest possible magnetic moment and is termed the *magneton* (see Chap. VII).

Selection Rule

The selection rule (*Auswahlregel* in German) is due to Rubinowicz and Sommerfeld (1918). To explain the significance of the rule we begin by recalling that for each atom there exists a series of numbers, the energy levels W , such that differences between $\frac{W_1}{h}$, $\frac{W_2}{h}$, etc. (the spectral terms), give the frequencies emitted. It turns out that certain of the frequencies obtainable by this process are, in practice, not observed. These correspond to so-called "forbidden" transitions. Consider, as an illustration, the case of sodium with energy levels -5.13 , -3.01 , -1.94 , -1.51 , -1.38 , -1.02 , etc. The transition from the state -5.13 to -3.01 occurs, and so also does the transition -5.13 to -1.38 , but the transition -5.13 to -1.94 is not observed (see p. 79). In other words, if the levels are grouped into columns, as shown in Fig. 13, it is found that the only possible transitions are those effected between levels belonging to *adjacent* columns. It is clear that a process of *selection* is in operation here.

The first selection rules were justified by Rubinowicz and Sommerfeld by applying the theorem of the *conservation of moment of momentum* to the process of emission of an electromagnetic radiation. Other rules were deduced with the aid of Bohr's correspondence principle. Actually the selection rules are obtained, by a rigorously deductive method, in wave mechanics by making use of perturbation theory. We shall return to this subject in the next section.

More Complex Atomic Spectra. The Rotating Electron. Multiplet Lines

Examination of the spectra of atoms containing several electrons external to the nucleus (atoms more complex than hydrogen) has shown that in grouping the individual lines into spectral series and in the general classification of such spectra, a single quantum number n (analogous to the total quantum number of hydrogen) is not sufficient.

The spectral terms W/h , and hence the energies W of the stationary states of the atom, must depend in general on 4 "quantum numbers" (indices or variables assuming integral values). Excluding phenomena characteristic of the nucleus (*e.g.*, the nuclear magnetic moment), these four numbers or parameters suffice for the complete classification of atomic spectra and for a rational interpretation (or even derivation) of the structure of the periodic system of the elements (see p. 139).

This classification and interpretation were only arrived at by degrees and after many attempts. Among the physicists who have contributed in greatest measure to the accomplishment of this really monumental task we may mention Landé, Bohr, Pauli and Sommerfeld. A theoretical justification, *a posteriori*, of their conclusions has been obtained, almost without special effort, as a bye-product of the masterly investigation of P. A. M. Dirac on the relativistic theory of the electron.

We limit ourselves to giving a brief outline of the results obtained.

For each extra-nuclear electron it is permissible to assume, as a first approximation, that its motion takes place in a central field of force. Quantum mechanics shows that the energy of binding of such an electron in a stationary state of the atom, depends on four parameters :

- n — the *principal* or *total* quantum number,
 - l — the *azimuthal* quantum number.
 - m — the *magnetic* quantum number,
 - s — the quantum number of the "electron spin."
- (The definition of this will be given shortly.)

The first of these assumes positive integral values and corresponds to the quantum number which in the hydrogen atom fixes the energy in the formula :

$$W = - \frac{2\pi^2 m_0 e^4}{h^2 n^2}.$$

The azimuthal quantum number measures in units of $\frac{h}{2\pi}$, the *angular momentum* or *moment of momentum* of the *orbital* motion of the electron with respect to the centre of force. Having fixed the total quantum number n , the azimuthal quantum number l can assume only the following n values,

$$0, 1, 2 \dots \overline{n-1}.$$

The *magnetic* quantum number m appears in the expression for the energy when there is an external magnetic field. For given n and l , the number m can assume only the $(2l+1)$ values,

$$-l, -(l-1) \dots -2, -1, 0, 1, 2 \dots (l-1), l.$$

Finally, s , the quantum number of the electron rotation, can have only the values,

$$-\frac{1}{2}, +\frac{1}{2}.$$

These rules, as well as the exact definitions of the four quantum numbers, can be derived only from the quantum mechanics theory of the motion of an electron in a central field. The quantisation rules of quantum mechanics lead naturally both to the consideration of the four quantum numbers cited above and to the introduction of the very fruitful hypothesis of the rotating electron. We shall give a brief explanation of the significance of the latter.

According to two young Dutch physicists, Uhlenbeck and Goudsmit,* the electron, in addition to its charge e and its mass m_0 , has associated with it a magnetic moment μ_0 of amount one Bohr magneton,

$$(\mu_0 = \frac{eh}{4\pi m_0 c} = 0.91 \times 10^{-20} \text{ absolute electromagnetic units}),$$

* *Naturwissenschaften*, 13, p. 953, 1925.

and an angular moment of amount $\frac{1}{2} \frac{h}{2\pi}$, in the same direction as the magnetic moment, but in the opposite sense (a consequence of the negative charge of the electron). A possible interpretation is to regard the electron as a particle, carrying electric charge and rotating about an axis through the centre of gravity. Hence the term *rotating electron* by which the hypothesis is usually known.

Of the reasons which led to the introduction of the spinning electron, the most important was that, in the absence of some such hypothesis, the quantum rules predicted only half as many energy levels as were actually found spectroscopically. The levels predicted were those dependent on the three quantum numbers n, l, m :

$$W = W(n, l, m).$$

With the introduction of the spinning electron a new quantum number made its appearance, capable of assuming two values only, $+\frac{1}{2}$ and $-\frac{1}{2}$. As a consequence, the number of energy levels is doubled. We have

$$W = W(n, l, m, s).$$

In Dirac's relativistic quantum theory of the electron, the special hypothesis of electron spin is unnecessary. The characteristics of electron spin are derived as a corollary from the invariance of the quantum equations with respect to Lorentz transformations.

What then are the problems which the new idea is capable of resolving? As already mentioned, its principal success is in the classification of atomic spectra and, in particular, in the explanation of the complex structure of multiplet lines as well as in the interpretation of the Zeeman effect for such lines (improperly called the *anomalous Zeeman effect*).

In addition, various problems connected with the formation of molecules of the type known as "homopolar", and the statistics of electrons (in particular the statistics of free electrons in metals), have received an adequate explanation by the introduction of the rotating electron and the Fermi statistics.

Multiplet lines originate in the following manner. In a quantum

transition between two energy levels W_1 , and W_2 , the quantum numbers l and m are subject to certain selection rules. In central fields, l can vary only in such a way that $\Delta l = \pm 1$,

whilst for m ,

$$\Delta m = \begin{cases} 0 \\ \pm 1 \end{cases}.$$

It is also found that the energy W depends almost exclusively on n and l , varying very little with change of m and s , so that for a given pair of values (n, l) there may be a number of levels having nearly the same energy values. It is clear then that the frequencies corresponding to levels which differ in s or in m (for each of the extreme levels) will also lie close together and will form groups of lines. These groups are termed *multiplets* (*doublets*, *triplets*, . . .) when the spectral terms of the individual components of the group differ only in the value of the quantum number s of the valency electrons. In a magnetic field there occurs a further subdivision of the multiplets, due to variation in the magnetic quantum number m . Both the normal and the anomalous Zeeman effect originate in this way. In the next paragraph we give a brief description of the anomalous Zeeman effect.

The Anomalous Zeeman Effect * †

Following on Zeeman's discovery (1896), the experimental and theoretical study of the effect of magnetic fields on radiating atoms has been energetically pursued, and constitutes in fact one of the most powerful methods of spectroscopic investigation.

Of the 92 elements of the periodic systems, 57 have been subjected to magnetic fields whilst radiating, and in order to obtain the maximum amount of information by this kind of analysis, the experimentalists have employed interferometers of very high resolving power (Michelson, Fabry, Lummer) and the most powerful magnetic fields obtainable.

* The adjective "anomalous" is not very appropriate as it is the so-called *anomalous* effect, which is usually observed. The qualification arose from the fact that Lorentz's original explanation, although applicable to the subdivision of lines into triplets with the correct separation, failed to account for the configurations which we are about to describe.

† Paschen and Back, "Normale und anomale Zeemaneffekte," *Ann. d. Phys.*, 391, p. 897, 1912, and 40, p. 960, 1913.

As regards the latter, Kapitza, working at Cambridge, has recently realised a field of 320,000 gauss, acting for a brief interval of time, of the order of a hundredth of a second. This work provides a good example of the powerful aids which electrotechnics can to-day place at the disposition of the physicist investigating atomic problems.

The so-called anomalous Zeeman effect is characterised by the appearance of a greater number of lines than the three components

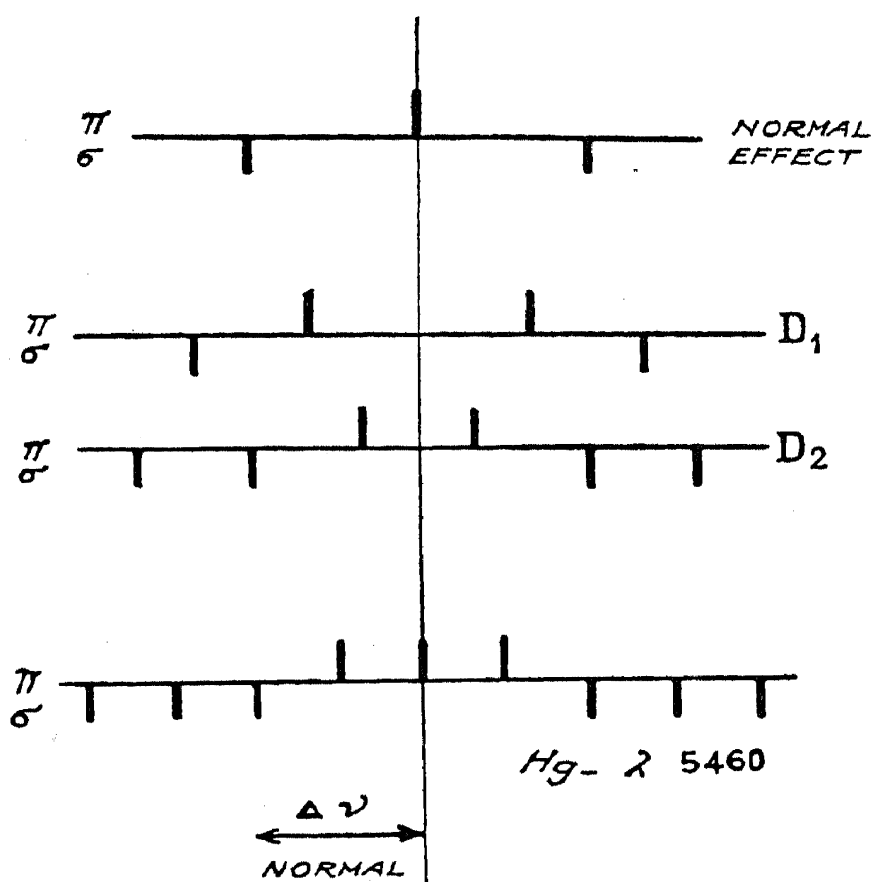


FIG. 27.

of the normal effect. The latter is in reality observed only when the original line is simple, each of the components in a multiplet giving rise to several lines.

The effect of a magnetic field can be described as a substitution of several stationary states, in place of each original state. Thus from the purely descriptive standpoint, to specify one of these states we require four parameters, namely, the three quantum numbers n , l , s , of the original state and a fourth quantum number m denoting position in the group formed when the field is applied.

Again, however, it is observed that, coupling together in pairs in all possible ways the states which emerge as a result of the field, not all the corresponding frequencies are possible, *i.e.*, some are missing from the spectrum. Once more we are obliged to invoke a selection rule to supply an explanation of the facts.

The inter-line separations in the group generated by subdivision under the influence of the magnetic field are proportional to the field strength. Actually in the case of the anomalous Zeeman effect this is true only for fields of not too great an intensity, for, with very powerful fields, the subdivision of the lines of a multiplet changes radically and the pattern merges into a normal triplet, just as though the multiplet were replaced by a single master line. This effect is known as the *Paschen-Back effect*. By non-intense fields we mean here magnetic fields producing a Zeeman separation of approximately the same amount as the distances between lines in the original multiplet.

In Fig. 27 are given sketches of the lines derived from the sodium doublet D_1D_2 and from a mercury line. The symmetry of the patterns should be noted. Components polarised parallel to the field direction are shown above the horizontal line, those polarised perpendicular to the field, below it.

We are faced with the necessity of explaining why so many lines are formed and why the distances between the lines differ from the value appropriate to the normal effect. Furthermore, it has to be shown why, with increase of field intensity, the relative separations change in accordance with the Paschen-Back effect.

In the explanation of the multiplets it was supposed that the various states belonging to a single group were different because of different orientations of the rotating electron or electrons (valency electrons). It will now be assumed that the various states which replace a given single state when the atom is in a magnetic field are distinct on account of different orientations of the *resultant angular momentum*, either of the *orbital* motion or of the *electron spin*, with respect to the field direction.

As we have seen, an electron moving round in an orbit with

angular momentum P is equivalent to a magnet moment M proportional to P , in fact, $M = \frac{Pe}{2m_0c}$. Both P and M are vectors normal to the plane of the orbit and are therefore parallel.

If several electrons are moving in different plane orbits about the same nucleus, their individual angular momenta add up vectorially to give the angular momentum of the whole system and similarly the component magnetic moments give the magnetic moment of the system. The two vector sums are parallel and their absolute values are related by the equations just given.

It is found that certain of the groups or internal shells of electrons form configurations of zero resultant angular and magnetic momentum. Such groups are termed *closed*. The electrons external to the outermost closed shell are known as the *valency electrons* or *optical electrons*, because it is these which determine the chemical and electrochemical valency, as well as the type of spectrum. In the theory of optical spectra, only these electrons need to be considered.

As already explained, the atom in an external magnetic field can set itself only in a few isolated orientations, which are such that the projections of the magnetic moment (or the angular momentum) differ by a fixed amount. Also, transitions are permissible only between *adjacent* states. We have in fact stated the selection rule valid for the magnetic quantum number m , which fixes the projection of the resultant magnetic moment on the field direction : $\Delta m = 0, \pm 1$. Recalling the rule which limits the range of values of m , $|m| \leq l$, it is clear that to every term defined by the three quantum numbers n, l, s , there will correspond in a weak magnetic field exactly $(2l + 1)$ terms, because the quantum number m , associated with the projection of l on the field direction, can assume the values,

$$l, l - 1, l - 2, \dots, 1, 0, -1, \dots, -(l - 1), -l.$$

This theory due to Landé leads therefore to the prediction of a multiplicity of stationary states, and it is seen how the hypothesis of *orientation* applied to multiplets is perfectly demonstrated in the anomalous Zeeman effect.

Up to this point no attention has been paid to the fact that the various stationary states replacing the original state as a result of the applied field are not spaced at intervals of amount $Hh\omega$,* which is the value appropriate to the normal effect. Actually, in the anomalous effect, the difference between the stationary states is given by $\Delta U = g\omega h$ and the factor g varies in general between $\frac{1}{2}$ and 2. This fact, which represented a serious difficulty for Landé's theory, was completely explained by the aid of the spinning electron hypothesis.

Back and Landé in 1923 succeeded in giving the complete scheme of line separations, which are expressed in every case by the formula :

$$\Delta\nu = m\omega g.$$

$\Delta\nu$ is the frequency difference between two consecutive lines : m can assume the values $j, (j-1), (j-2) \dots -j$ and g is the so-called splitting factor (Aufspaltungsfaktor) which is given by a table or by an empirical formula discovered by Landé himself, in terms of j, s, l . For the combinations of the terms the rules $\Delta m = 0$ or $\Delta m = \pm 1$ with $\Delta m = 0$ if $\Delta j = 0$, hold good.

We give in the following Table as examples the g values for triplets and quartets :

Values of g

	$j = 0$	1	2	3	4	5	$j = \frac{1}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{7}{2}$	$\frac{9}{2}$	$\frac{11}{2}$
Values of l	Triplets $s = 1$						Quartets $s = \frac{3}{2}$					
0		2					2					
1	$\frac{0}{0}$	$\frac{3}{2}$	$\frac{3}{2}$				$\frac{8}{3}$	$\frac{2}{15}$	$\frac{8}{5}$			
2		$\frac{1}{2}$	$\frac{7}{6}$	$\frac{4}{3}$			0	$\frac{6}{5}$	$\frac{4}{35}$	$\frac{10}{7}$		
3			$\frac{2}{3}$	$\frac{1}{12}$	$\frac{5}{4}$			$\frac{2}{5}$	$\frac{3}{35}$	$\frac{7}{8}$	$\frac{4}{3}$	
4				$\frac{3}{4}$	$\frac{2}{10}$	$\frac{6}{5}$			$\frac{4}{7}$	$\frac{6}{8}$	$\frac{11}{9}$	$\frac{14}{11}$

* Where $\omega = \frac{eH}{4\pi m_0 c}$. The velocity of the Larmor rotation is $\frac{eH}{2m_0 c}$ and the Larmor frequency is therefore $\frac{eH}{4\pi m_0 c}$.

The splitting factor g is determined from j, s, l , in each case using the important empirical formula of Landé, which it is now possible to deduce in a perfectly natural way using quantum mechanics.

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad . \quad . \quad . \quad (1)$$

The model adopted for the angular momenta will now be given. From it we can derive an expression for $\Delta\nu$ of the form given above,

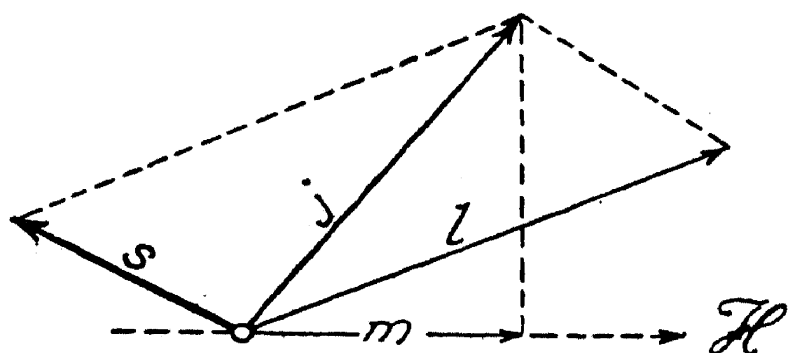


FIG. 28.

but it is only possible to deduce the correct formula (1) for g , by having recourse to the quantum mechanics of Heisenberg. Using the mechanical model (Fig. 28), we obtain for g a result which approaches the correct

form, although differing from it in an essential detail.

The energy associated with the moment j is clearly,

$$h \cdot \Delta\nu_1 = h\omega j \cos(jH) = h\omega m.$$

If the energy relative to s can be determined, then summing the two energies and dividing by the quantum constant h , we shall arrive at $\Delta\nu$. Now the vector s in a weak magnetic field precesses about j , and j in turn precesses about the field direction. Hence,

$$h \cdot \Delta\nu_2 = h\omega s \cos(s, j) \cos(j, H) = h\omega s \cos(s, j) \cdot \frac{m}{j}.$$

Since

$$\cos(s, j) = \frac{j^2 + s^2 - l^2}{2js},$$

it follows that,

$$h\Delta\nu_2 = h\omega m \frac{j^2 + s^2 - l^2}{2js}.$$

The distance, in frequency, of the terms emerging as a result of the field is therefore, according to the simple model adopted here,

$$\Delta\nu = \omega m \left[1 + \frac{j^2 + s^2 - l^2}{2js} \right]$$

and it is clear that, for large values of l and s , the factor in brackets reduces to the exact result given in (1) above.

This calculation shows at once that Landé's formula can only be valid for the case when the magnetic field is weak so that the disposition of the vectors l and s is not disturbed. An intense field will act separately on these two vectors, giving rise to the Paschen-Back effect.

We can now give a more detailed explanation of the fact indicated earlier, that simple spectral lines show the *normal* Zeeman effect. The reason is that the two levels determining the radiation emitted, being both simple, possess total electron magnetic moment zero, *i.e.*, $s = 0$, and hence $j = l$ and $g = 1$. Thus the total energy of the atom in the field H is

$$\begin{aligned} W_0 + mH\mu_0 & \text{ in one level,} \\ W_0' + m'H\mu_0 & \text{ in the other level,} \end{aligned}$$

and the frequency emitted will be,

$$\frac{W_0 - W_0'}{h} + (m - m')H\frac{\mu_0}{h} \text{ instead of } \frac{W_0 - W_0'}{h}.$$

By the selection rule, $m - m' = \begin{cases} 0 \\ -1 \\ +1 \end{cases}$ and hence the normal Zeeman effect is obtained with the two lines displaced on either side by the frequency step $\nu_L = \frac{H\mu_0}{h} = H\frac{e}{4\pi m_0 c}$, which is the Larmor frequency.

Fine Structure of X-ray Spectra

The problem of the classification of the energy levels of X-ray spectra has also been satisfactorily solved by the introduction of suitable quantum numbers. Accurate measurements of X-ray spectra showed that the number of lines observed exceeded the number to be expected if the levels L, M, N, etc., were simple. It was necessary to explain the slight modifications of the various states giving rise to closely adjacent lines in the case of the groups L, M, N, O, P, but not K.

This necessity was also evident from researches on X-ray absorption edges (Vol. I, p. 247), which showed the L level to be a triplet, the M a quintuplet, etc. The levels K, L, M, N, O, P exhibited in all twenty-four different values. The same result emerged from the method of corpuscular spectra employed by Robinson, Ellis, de Broglie, Whiddington, which we shall discuss in a later section (p. 176). The solution of the problem of explaining in a

single scheme valid for all the elements, the origin of all the X-ray lines, was obtained in 1927, thanks principally to the work of four physicists : Smekal, Wentzel, Coster and Bohr.*

As the accompanying figure (Fig. 29) makes clear, every state is characterised by an azimuthal quantum number l and an internal quantum number j , in addition to the total quantum number n . The internal quantum number j corresponds to the

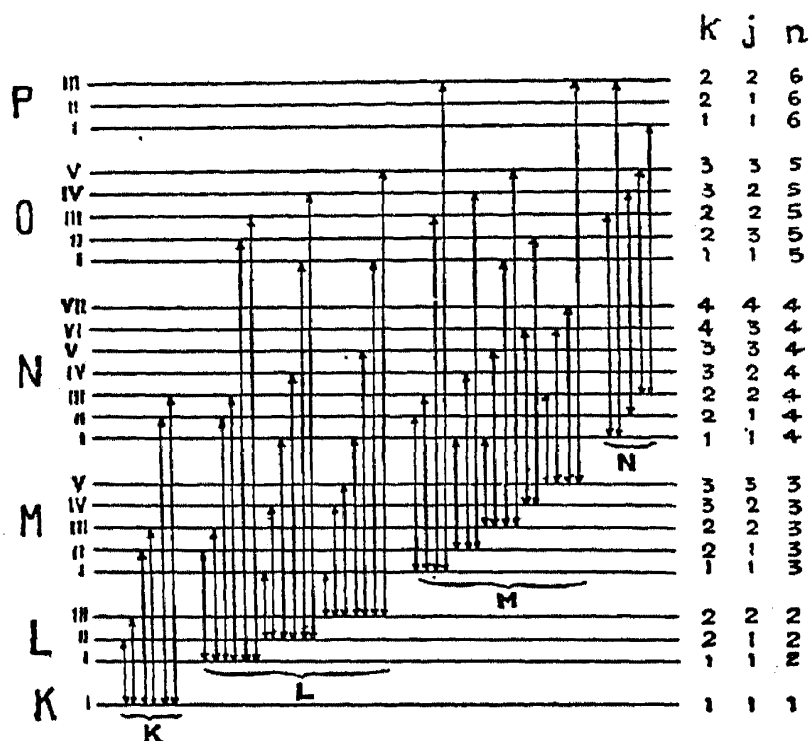


FIG. 29.

resultant angular momentum of the orbital motion of the electrons and their spin.

As already observed, $l = k - 1$ can assume values ranging from 0 to $n - 1$, and j takes integral values less than, or at most equal to k . By the selection rule, transitions can occur only subject to the conditions,

$$\Delta l = \pm 1 \quad \Delta j = \begin{cases} 0 \\ \pm 1 \end{cases}$$

The number of possible combinations between two states is thereby very considerably reduced, and the levels are restricted to twenty-four in all, as shown in the figure. Thus, in contrast to

* D. Coster, "On the Spectra of X-rays and the Theory of Atomic Structure," *Phil. Mag.*, 44, p. 546, 1922.

optical spectra only twenty-four levels are required to represent completely the X-ray lines of all substances.

Construction of the Periodic System. Pauli's Exclusion Principle (1925)

We come now to a development closely connected with Pauli's observation that the complete data of experimental spectroscopy demand the introduction of four quantum numbers. This development is the theoretical construction of the periodic system, that is to say, the construction of a rational theory of the

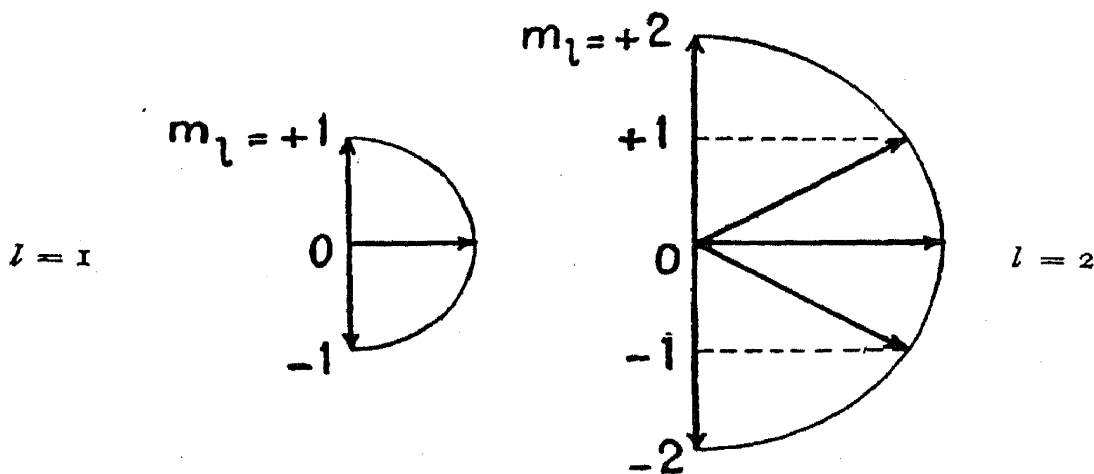


FIG. 30.

distribution of the electrons in successive atomic levels, taking account of the chemical and spectroscopic properties of the elements. It may be added that this theory leads exactly to the periodic table of Mendeleeff.

Previously, in defining the orbit of the optical electron we have used the total quantum number n , determining the energy and the azimuthal quantum number $l(l = k - 1)$. Then, with reference to an arbitrary preferred direction which may be represented as an external magnetic field, the latter vector, to comply with the hypothesis of spatial quantisation, can assume only certain special

directions, such that its projection m_l is a multiple of $\frac{h}{2\pi}$. For example, when $l = 1$ the permissible directions are three in number, $m_l = \pm 1$ or 0. For $l = 2$, five orientations are possible,

with $m_l = 2, 1, 0, -1, -2$, and in general there will be $(2l + 1)$ orientations (see Fig. 30).

There is, however, another conception which must be referred to in the present argument, and this concerns the electron itself. As explained, the electron possesses an angular momentum s which, omitting the factor $\frac{h}{2\pi}$, assumes the values $\pm \frac{1}{2}$. The vector s is orientated with respect to the preferred direction of the atom in the same way as the vector l , namely, in such a way that the difference of its projections has an integral value. In other words, s can assume only two positions, parallel and antiparallel to the preferred direction, for the difference between $+\frac{1}{2}$ and $-\frac{1}{2}$ is 1.

This brings us to Pauli's principle. What has been stated with respect to the optical electron to which four quantum numbers are attached, and which was nothing more nor less than an abstraction to assist us with a mechanical model, is extended to all the electrons of the atom. Pauli's *exclusion principle* * affirms that *every* electron orbit is completely characterised by four quantum numbers n, l, m_l, m_s (or by n, l, j, m) in such a way that a given set of values of these four quantum numbers defines one and only one orbit. This means that in no case can two electrons occupy the same orbit, or, in other words, no two electrons can exist in the same quantum state.

It would be desirable at this point to show how Pauli came to formulate his important principle (sometimes termed the *equivalence* principle), but to reproduce the argument would involve us in complicated details. We shall therefore limit ourselves to the remark that he perceived that the interpretation of the complete scheme of the successive formation of the atoms discovered by Stoner in 1924 (see p. 69) required the association of four quantum numbers ($n, l, m_l, m_s = \pm \frac{1}{2}$) with each electron, and, on the other hand, that having fixed these, the terms or energy levels of the atom were determined, and hence its spectrum. †

* W. Pauli, *Zeitschrift f. Physik.*, 31, p. 765, 1925.

† Thus, for example, for two, three, four electrons p to which correspond $l_1 = l_2 = l_3 \dots = 1$, there are formed the possible values of m_l and of

Thus, reversing the argument, it should be possible, starting from the terms furnished by spectroscopy, to work back to the sets of values of the four quantum numbers to be attributed to the individual electrons. The exclusion principle had its origin in investigations of this nature.

Consider now an electron in the K shell. For this electron $n = 1$, $l = 0$, and hence $m_l = 0$. Thus three of the four quantum numbers are fixed and the fourth can assume only the two values $+\frac{1}{2}$, $-\frac{1}{2}$. It is easy to see therefore that in the K shell there can be no more than two electrons. The atom with two electrons in the K shell completes the first period of the periodic system. This atom is helium, which has one closed electron shell and exhibits the properties of a noble gas, devoid of chemical affinity.

The same state of affairs holds good for the first subdivision of the L shell for which $n = 2$, since for $l = 0$, $m_l = 0$ and $m_s = \pm \frac{1}{2}$. Thus this shell may already contain two electrons before we come to the case $n = 2$, $l = 1$. Here there are three possible values for m_l , $m_l = \begin{cases} \text{zero} \\ \pm 1 \end{cases}$, and with each of these may be associated $m_s = \pm \frac{1}{2}$, so that there will be $2(2l + 1) = 6$ possible sets of values for the four quantum numbers, as shown by the following table :

$$\begin{array}{ccc|ccc} m_l = +1 & 0 & -1 & +1 & 0 & -1 \\ m_s = +\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \end{array}$$

The L shell is therefore closed (completed) when it contains $2 + 6 = 8$ electrons, and the eighth place after helium is occupied by an atom with $2 + 8$ electrons, the rare gas neon, which is an inert substance resembling helium.

We now come to the M shell. For $l = 0$ and $l = 1$ there will

$m_s = \pm \frac{1}{2}$, and then the values $m_l = \Sigma m_l$; $m_s = \Sigma m_s$. This method of obtaining m_l , m_s for the atom is based on the adiabatic invariance of the quantum numbers in the presence of a slowly varying magnetic field, even when the latter tends to zero.

In investigations on the spectral terms it is found that a *completed* electron shell can give rise only to a simple term, which explains why a great majority of the terms of a spectrum are determined solely by the electrons external to a closed shell (as, for example, in the case of the alkalis).

be in all $2 + 6$ combinations as before. For $l = 2$, the following $2(2l + 1) = 10$ additional possibilities appear :

$$\begin{array}{cccccc|ccccc} m_l = & 2 & 1 & 0 & -1 & -2 & 2 & 1 & 0 & -1 & -2 \\ m_s = & +\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} & +\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} & -\frac{1}{2} \end{array}$$

Thus the M shell, characterised by the total quantum number 3, is completed when it contains $2 + 6 + 10 = 18$ electrons, with the reappearance of a rare gas—argon. The numerical values of $2(2l + 1)$, the number of possible combinations, shown in the table below, determine the maximum number of elements corresponding to each shell.

Shell.	K.	L.	M.	N.	O.
$n =$	1	2	3	4	5
$l =$	0	0 1	0 1 2	0 1 2 3	0 1 2 3 4
$2(2l + 1) =$	2	2 6	2 6 10	2 6 10 14	2 6 10 14 18
	2	<u>8</u>	<u>18</u>	<u>32</u>	<u>50</u>

The totals 2, 8, 18, 32, 50, give the numbers of elements in the short and long periods. As mentioned earlier (Vol. I, p. 11), these numbers may be written in the form 2×1^2 ; 2×2^2 ; 2×3^2 ; 2×4^2 ; 2×5^2 .

We notice immediately that the O shell, whose systematic construction begins with hafnium, should contain 50 elements, not all of which actually exist. In reality, the construction of the shells is not effected completely as described above. It proceeds regularly up to argon, but then with potassium and calcium (20) the N shell begins to form before the completion of the preceding shell. The O shell is initiated irregularly with rubidium (37).

It should be noted that these deviations from the systematic building up of the electron shells concern only the less tightly bound, external electrons. Thus if we regard as representative of the elements not only the neutral atoms, but also the ionised atoms, the theoretical rule is found to be exactly verified. The ions are of course not familiar only to the chemist. They have

been extensively studied spectroscopically, particularly by Millikan and Bowen.

For the complete table, showing the distributions of the electrons in the various shells and sub-shells, see p. 69.

Thus the very important exclusion principle supplies the reason why the electrons of an atom do not all occupy the most stable orbit closest to the nucleus, but dispose themselves in different orbits, determining in this way the chemical properties which differentiate the elements one from another.

That the nuclear structure must also be subject to the Pauli principle has been established by G. Beck, of Vienna (1928). He arranges the isotopes revealed by Aston's well-known measurements, in a table from which certain simple arithmetical rules emerge, and these serve as a foundation for a theoretical construction of the nucleus.

The construction of the atoms throughout the periodic system on the basis of the quantum numbers relative to the various electrons, has made clear the special position occupied by the rare gases. The grouping of the electrons in the atoms of the rare gases is shown in the Table given below, in which the letters K, L, M, N, O, P, appearing in the headings, represent the successive shells (beginning from the innermost shell), for which $n = 1, 2, 3, 4, 5, 6$, respectively. Thus, M_{23} denotes $n = 3, l = 2, j = 3$. For each position, two electrons, corresponding to the two possible orientations of the rotating electron, are permissible.

Grouping of Electrons in the Atoms of the Rare Gases

Sub-Group.	K	$L_{01} \quad L_{12}$ L_{11}	$M_{01} \quad M_{12} \quad M_{23}$ $M_{11} \quad M_{22}$	$N_{01} \quad N_{12} \quad N_{23} \quad N_{34}$ $N_{11} \quad N_{22} \quad N_{33}$	$O_{01} \quad O_{12} \quad O_{23}$ $O_{11} \quad O_{22}$	$P_{01} \quad P_{12}$ P_{11}
Helium .	2					
Neon .	2	2 2 4				
Argon .	2	2 2 4	2 2 4			
Krypton .	2	2 2 4	2 2 4 4 6	2 2 4		
Xenon .	2	2 2 4	2 2 4 4 6	2 2 4 4 6	2 2 4	
Emanation .	2	2 2 4	2 2 4 4 6	2 2 4 4 6 6 8	2 2 4 4 6	2 2 4

The following Table is a condensed form of the above :

Rare Gases.	Principal Quantum Numbers of the Group.						Total Number of Electrons.
	1	2	3	4	5	6	
Helium .	2						2
Neon .	2	8					10
Argon .	2	8	8				18
Krypton .	2	8	18	8			36
Xenon .	2	8	18	18	8		54
Emanation .	2	8	18	32	18	8	86

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CHAPTER IV

SPECIFIC HEATS

LONG before the quantum ideas were consolidated into a coherent theory, Einstein (1911) used Planck's original notion of the quantised oscillator to explain the temperature variation of specific heats. As we saw in Chap. II, Bohr's first applications of quantum ideas were made in 1913.

As in the case of gases, it is necessary, in the first place, to distinguish between the specific heat at constant pressure and the specific heat at constant volume, the difference between the two corresponding to the external work which is done when the substance is allowed to expand during the temperature rise. If, as is usual, it is the specific heat at constant pressure which is determined, then in passing to the other specific heat the necessary correction must be made.

It was in 1911 that Nernst and his collaborators in Berlin undertook their now famous specific heat determinations extending over all the temperature intervals obtainable in the laboratory. It was found that, whilst at high temperatures the specific heats of solids actually had the theoretical value 5.95 calories per gramme atom for all substances (aluminium, lead, copper, silver, etc.) towards the absolute zero of temperature, all the specific heats tended to the value zero.

Variation of the Specific Heats of Solids with Change of Temperature. The Quantum Theory Interpretation

We saw in Vol. I, Chap. III, in discussing the specific heats of solid bodies, that the average kinetic energy of the molecules at the temperature T has the value $\frac{3}{2} RT$ for a monatomic substance.

Since the potential energy for a gramme molecule of the solid body is also given by $\frac{3}{2}RT$, it follows that the specific heat at constant volume, *i.e.*, the quantity of heat required to raise the temperature one degree, should have the value $C_v = R$ in ergs. or 5.95 calories per gramme atom.*

Thus the specific heats of all substances in the solid state, referred to an amount of one gramme atom, should be about 6 calories for monatomic substances. In particular this should be the case for the metals, which may properly be considered monatomic.

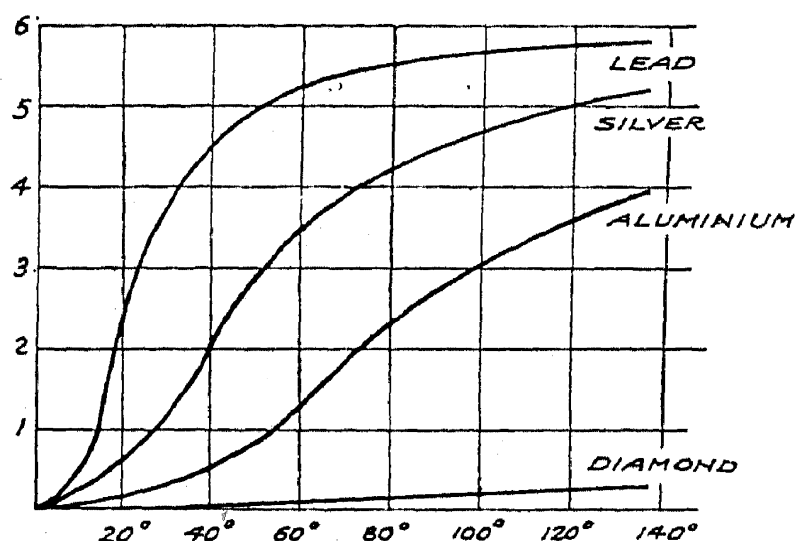


FIG. 31.

as pointed out above, that the specific heats of solids tend towards the value zero when the absolute zero is approached. The variation of C_v with change of temperature is depicted for a number of elements in Fig. 31.

All the curves are similar. Moreover, if the temperature scale is changed, the curves can be made to coincide. For example, taking the curve for silver and compressing the temperature scale in the proportion 1 : 2.3, a curve identical with that of lead is obtained. Similarly, a compression in the proportion 1 : 4.1 transforms the curve for aluminium into the lead curve.

The immediate deduction is that the theory (based on classical mechanics), according to which the specific heats of all the

* 4.19×10^7 ergs are equivalent to 1 calorie.

This is the celebrated law of Dulong and Petit. It gives only approximate agreement with experiment, the agreement being better at high temperatures. Experimentally we know that the specific heat is a function of temperature, and Nernst's measurements at low temperatures have shown,

elements should equal 5.95, is applicable at high, but breaks down at low, temperatures.

Einstein, introducing the ideas put forward by Planck, arrived at the general law of specific heats. For this purpose it is necessary to regard the atoms of a monatomic solid as Planckian oscillators, for which the average energy, as seen in Chap. I, has the value,

$$W = \frac{N h \nu}{e^{\frac{h \nu}{R T}} - 1}.$$

For atoms oscillating with three degrees of freedom, the energy is three times this amount. Writing for brevity :

$$\beta = \frac{N}{R} h = \frac{6.55 \times 10^{-27} \times 6.06 \times 10^{23}}{0.8316 \times 10^8} = 4.77 \times 10^{-11}$$

we obtain for the total energy $W = N w$,

$$W = N w = \frac{3 R \beta \nu}{e^{\frac{\beta \nu}{T}} - 1}.$$

The specific heat is merely the derivative $\frac{dW}{dT}$, and hence we obtain :

the specific heat at constant volume

$$C_v = 3R \frac{e^{\frac{\beta \nu}{T}} \left(\frac{\beta \nu}{T} \right)^2}{\left(e^{\frac{\beta \nu}{T}} - 1 \right)^2} \quad \text{Einstein's formula.}$$

The curves representing C_v for the various simple monatomic substances are obtained by attributing appropriate values to the frequency ν , one value for each element considered.

It is easy to verify that for sufficiently high temperatures Einstein's formula corresponds sensibly to $C_v = 3R$, as it should do. The different values of the parameter ν result in the curves for various solid elements departing dissimilarly from the simple law $C_v = 3R$.

Whilst the classical theory leads to the result that the specific

heat C_v equals $3R$, Einstein's theory furnishes a value which is a function of temperature, as demanded by experiment. From the qualitative standpoint, this is a great improvement. It remains to be seen if the results of the theory are satisfactory in their quantitative aspects.

Einstein verified his formula in the case of diamond. He used the experimental value of the specific heat at 331° absolute to derive the frequency ν , and then employed this value of ν in applying the formula to high temperatures. Actually the experimental values refer to the specific heat at constant pressure, but the difference is very small. We give some numerical values for diamond.

Specific Heat of Diamond

Absolute Temperature.	$T/\beta\nu$.	C_v Calculated from Einstein's Formula.	C_p Observed.
222.4	0.1679	0.762	0.76
283.7	0.2141	1.354	1.35
331.3	0.2500	1.838	1.84
413.0	0.3117	2.661	2.66
520.0	0.3924	3.631	3.63
1258.0	0.9493	5.507	5.51

Measurements of C_p at low temperatures down to 30° absolute have been made by Nernst, who found that the thermal capacity of diamond already approaches zero at about 50° absolute.

For diamond Einstein's formula appeared to represent faithfully the experimental facts. Such perfect agreement was lacking in other cases. At very low temperatures the formula tends to give too low values. In 1912 Debye gave the reason for this and perfected Einstein's theory.* The general formula at which he arrived is certainly the most satisfactory, as it interprets almost perfectly the experimental data for every substance and at all temperatures.

* Other work on this subject is due to Born and Karman, *Phys. Zeits.*, 13, 1912; 14, 1913; 15, 1914.

Einstein had also realised that by introducing one frequency only, he could obtain only an approximate expression for the specific heat, because a condensed substance possesses a complete spectrum of frequencies.

Before giving a brief exposition of Debye's work, it will be well to indicate how the vibration frequencies characteristic of a solid are determined.

One method depends on the use of *residual rays*. Many substances exhibit *selective reflection*, *i.e.*, they reflect preferentially rays having a certain wave-length. It is these most strongly reflected rays which are most powerfully absorbed when light is transmitted through the substance.

Thus if an incident beam comprising rays of all wave-lengths—for example, the radiation emitted by a black body at a high temperature—is reflected successively at several surfaces of the substance under examination, at each reflection the beam becomes more homogeneous and tends, in the limit, to contain only radiation of the frequency ν characteristic of the reflecting substance.

Another method for finding ν , due to Einstein himself, is based on the mechanical property of compressibility which bears a certain relation (involving also the atomic volume and atomic weight) to the vibration frequency. For the sake of brevity we omit the description of this method, but a little further on we shall explain how Lindemann has succeeded in relating the characteristic vibration frequency with the melting point.

These characteristic frequencies, determined in one way or another, are of the order, 10^{12} . For example, for silver $\nu = 4.4 \times 10^{12}$, for copper $\nu = 6 \times 10^{12}$, and for aluminium $\nu = 8 \times 10^{12}$.

Debye's Theory *

Einstein, to simplify the problem, had assumed that the vibrating particle (the atom) would give rise to only one monochromatic radiation of frequency ν , and would be capable of absorbing this radiation only. Debye, on the other hand, realised

* *Annalen der Physik*, 39, p. 789, 1912.

that the atoms of the solid would not execute free or independent vibrations, but that the motion of each particle would have an effect on the neighbouring particles. As a result, instead of one vibration frequency, there would be a complete spectrum, the vibrations of the system comprising the simultaneous motions of all the atoms. A conception of this kind certainly approaches more closely to reality.

The complete motion of the system can be analysed in the following manner. The first question we must ask is, how many vibrations are developed in a gramme of material, with wave-lengths lying between λ and $(\lambda + d\lambda)$. In answering this question it must be recalled that, whilst in the ether there occur the transverse electromagnetic oscillations, and, on the other hand, in the transmission of sound through a gas the oscillations are exclusively longitudinal, a solid is capable of maintaining vibrations of both kinds. The total number of stationary vibrations in a volume θ , and with wave-length between λ and $(\lambda + d\lambda)$, is given by $12\pi\theta\lambda^{-4}d\lambda$.

It would lead us too far away from our main topic to give the complete proof of this result, and we limit ourselves to the remark that considerations of physical dimensions *require* $\frac{\theta}{\lambda^4} d\lambda$ to be a pure number, and it follows that the number of vibrations must be proportional to λ^{-4} as written. Detailed analysis establishes that for the sound vibrations in a gas (longitudinal waves), the number is given by $\frac{4\pi}{\lambda^4} d\lambda$, for transverse vibrations (ether), by $\frac{8\pi}{\lambda^4} d\lambda$; and, finally, for a solid the total number of vibrations in the prescribed wave-length interval is equal to $\frac{12\pi}{\lambda^4} d\lambda$.*

In our case we refer the specific heat to a gramme molecule of the substance, containing N atoms. These taken together possess $3N$ degrees of freedom, whatever the volume occupied, which we may take to be unit volume. The velocity of propagation V_1 being the same for all transverse vibrations, the number of the

* A complete proof is given at the end of the chapter.

latter may also be expressed as $\frac{8\pi}{V_1^3} \nu^2 d\nu$, remembering that $\lambda = \frac{V_1}{\nu}$. In addition to the transverse waves (distortional waves), the solid may transmit longitudinal waves (compressional waves), like those of sound. The number of these is $\frac{4\pi}{V_2^3} \nu^2 d\nu$, where V_2 denotes their velocity of propagation. If we determine by addition the total number of vibrations of all kinds over the complete range of frequencies, the result will equal $3N$, the number of degrees of freedom of the N atoms.

Thus the number of vibrations of frequency between ν and $\nu + d\nu$, for the N atoms is given by :

$$\frac{8\pi}{V_1^3} \nu^2 d\nu + \frac{4\pi}{V_2^3} \nu^2 d\nu. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In this analysis of the complex motion of the atoms into trains of harmonic waves, Debye makes the very natural supposition that these $3N$ vibrations extend from zero frequency to a certain maximum frequency ν_m the latter being determined by the condition :

$$3N = 4\pi \left(\frac{2}{V_1^3} + \frac{1}{V_2^3} \right) \int_0^{\nu_m} \nu^2 d\nu \quad . \quad . \quad . \quad . \quad (2)$$

which expresses the fact that the total number of possible vibrations equals $3N$.

Integrating on the right-hand side, we obtain,

$$3N = \frac{4\pi}{3} \left(\frac{2}{V_1^3} + \frac{1}{V_2^3} \right) \nu_m^3 \quad . \quad . \quad . \quad . \quad (3)$$

At this point we recall that each vibration of frequency ν possesses energy of amount given by Planck's formula,

$$\text{mean energy of an oscillator} = \frac{h\nu}{e^{\frac{Nh\nu}{RT}} - 1} \quad . \quad . \quad . \quad . \quad (4)$$

The *total energy absorbed by the body* is given by the integral of the product of the mean energy corresponding to the frequency ν and the number of vibrations of this frequency, namely,

$$4\pi \left(\frac{2}{V_1^3} + \frac{1}{V_2^3} \right) \nu^2 d\nu = 9 \frac{N}{\nu_m^3} \nu^2 d\nu.$$

Thus :

$$\text{total energy} = \int_0^{\nu_m} 9hN \frac{1}{e^{\frac{Nh\nu}{RT}} - 1} \left(\frac{\nu^3}{\nu_m^3} \right) d\nu \quad \dots \quad (5)$$

The further steps in the calculation are given in the footnote,* bearing in mind that the aim of the theory is to evaluate the specific heat C_v , which is given simply as the derivative $\frac{dE}{dT}$.

* Putting, for brevity . . . ,

$$\xi = \frac{Nh\nu}{RT} \text{ and } \theta = \frac{Nh\nu_m}{R}$$

(5) becomes

$$\text{Energy} = E = 9RT \left(\frac{T}{\theta} \right)^3 \int_0^{\theta/T} \frac{\xi^3}{e^\xi - 1} d\xi$$

and differentiating with respect to T :

$$C_v = \frac{dE}{dT} = 3R \left[- \frac{\frac{\theta}{T}}{e^{\frac{\theta}{T}} - 1} + \frac{12}{\left(\frac{\theta}{T} \right)^3} \int_0^{\theta/T} \frac{\xi^3}{e^\xi - 1} d\xi \right].$$

For *high temperatures* the first term in the bracket reduces to -3 and the second becomes :

$$\frac{12}{\left(\frac{\theta}{T} \right)^3} \int \xi^2 d\xi = \frac{12}{\left(\frac{\theta}{T} \right)^3} \cdot \frac{1}{3} \left(\frac{\theta}{T} \right)^3 = 4$$

Hence $C_v = 3R$, as it should be, since at high temperatures the theory must pass over into the classical result.

On the other hand, at *low temperatures* we must develop the integral :

$$\int_0^\infty \frac{\xi^3}{e^\xi - 1} d\xi$$

in a series, from which we obtain the value 6.494. The first term now vanishes so that,

$$C = 3R \frac{12}{\left(\frac{\theta}{T} \right)^3} \times 6.49$$

and finally :

$$\frac{C_v}{\text{Classical Specific Heat}} = 77.94 \frac{T^3}{\theta^3},$$

or, written in another way,

$$C_v = 234 \frac{T^3}{\theta^3}.$$

The important result obtained takes the following form :
at very low temperatures

$$\frac{C_v}{3R} = 77.94 \frac{T^3}{\theta^3}.$$

As the absolute zero is approached it is clear that the specific heat does in fact vanish.

At low temperatures, therefore, the atomic heat of a solid substance is proportional to the cube of the absolute temperature, a result which Schrödinger * has conclusively verified for various substances in a temperature range extending from 20° to 50°

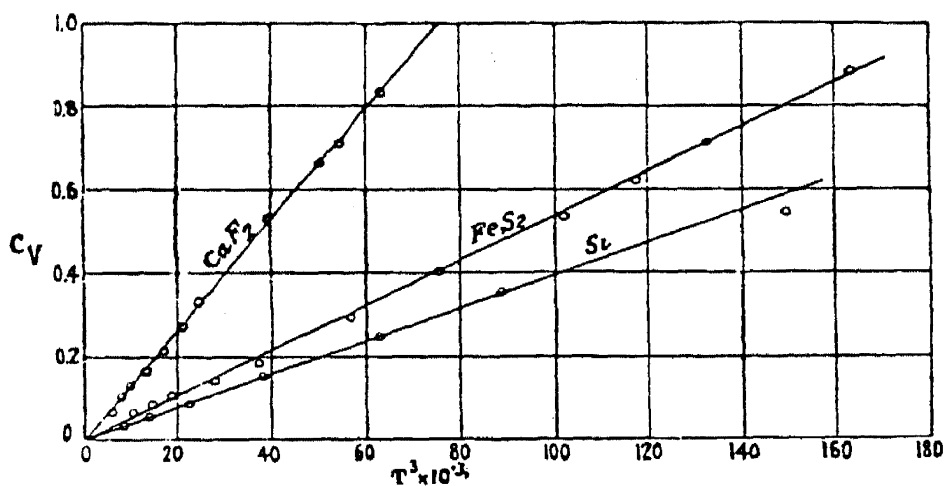


FIG. 32.

absolute. Plotting C_v against T^3 , straight lines through the origin are obtained (Fig. 32).

It is seen on examination that the general expression for the specific heat is a function of $\frac{Nh\nu_m}{RT}$ and this explains perfectly the fact that the curves giving the variation of C_v with temperature for different substances are not only similar, but can be made identical by a suitable modification of the temperature scale (see Fig. 33).

To arrive at the form of the typical curve, from which the curves representing the specific heats of all substances are derivable, we must assign an arbitrary value to the quantity

$\theta = \frac{Nh\nu_m}{R}$.† For example, we may put $\theta = 396^\circ$ and obtain the

* *Phys. Zeitschrift*, 20, p. 498, 1919.

† This quantity is a temperature.

curve of Fig. 33, which coincides with the experimental data for aluminium, on which the curves for copper and silver can be superposed by appropriate changes in the scale of the abscissa.

By suitably choosing the value of $\frac{Nh\nu_m}{R}$ the experimental curves of the metals aluminium, copper, silver, lead, etc., are obtained.

Subsequent to the publication of Debye's celebrated paper, experiments on copper at temperatures very near to the absolute

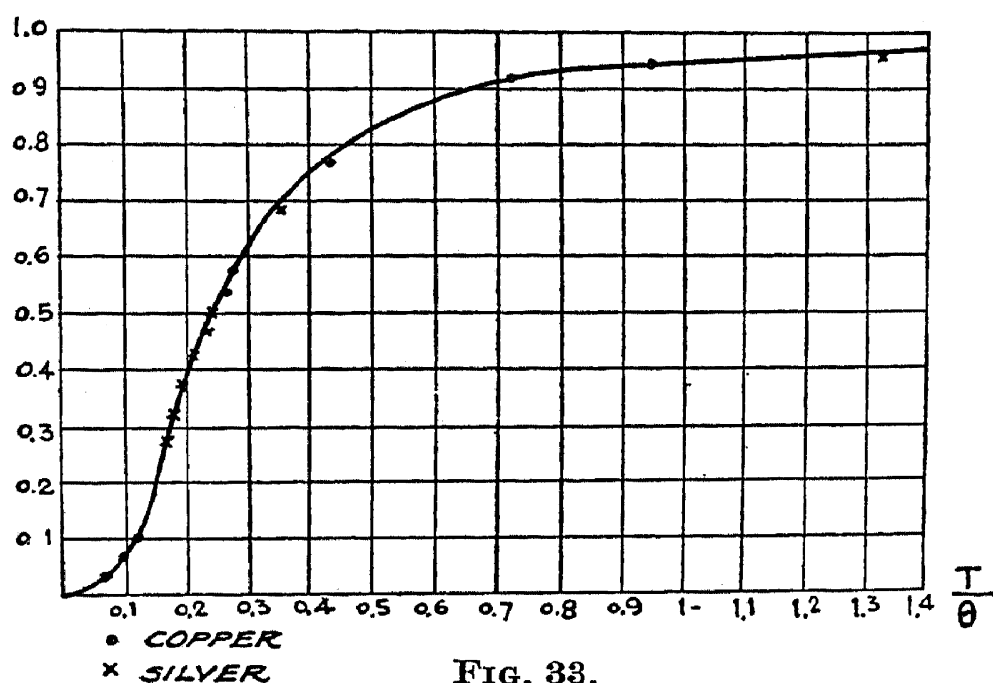


FIG. 33.

zero showed complete agreement with the predictions of the theory.

At the lowest temperatures the theory indicates that the specific heat C_v should vary with the cube of T . The experiments of Keesom and Kamerlingh-Onnes gave for copper :

at a temperature of 14.51° abs. $C_v = 0.0396$ $C_v/T_3 = 1.30 \times 10^{-5}$

„ „ 15.59 „ „ $= 0.0506$ „ $= 1.34$ „

„ „ 17.17 „ „ $= 0.0687$ „ $= 1.36$ „

The extraordinary delicacy of these measurements may be imagined.

That is not all, however. It has been seen that by a suitable choice of the constant $\frac{Nh\nu_m}{R}$ the specific heat curve of a substance can be represented by means of Debye's formula. The frequency

ν_m occurring in this constant can be deduced from other phenomena such as the elasticity of the substance. Hence it should be possible to construct, *a priori*, the specific heat curve for a solid element (silver, diamond, etc.) and we ought to find Debye's law verified.

This was done, and it was found that *the constant* $\frac{Nh\nu_m}{R}$ *which can be deduced from the experimental curve coincides with that furnished by elasticity data for the solid.* For example, for copper the value of $\frac{Nh\nu_m}{R}$ derived as a mean, from the experiments quoted above, equals 326.8, whereas the theory of elasticity leads to the value 326.

It only remains now to offer a few words of explanation concerning the elastic constants. A reader acquainted with the subject of "strength of materials" will know that in all the calculations connected with such problems the notion of modulus of elasticity (force producing unit deformation) enters. Another important quantity is the ratio of the extension to the lateral deformation of a body subjected to tension. Debye showed how from these data, together with the atomic weight and the density, the frequency ν_m could be calculated.

Also, Lindemann, two years before the appearance of Debye's theory, had given a formula (empirical as regards its precise form), which represents very well the values of ν_m for the elements examined. If T in degrees absolute is the melting point of the substance, m its atomic weight, V its atomic volume, it appears that the maximum frequency ν_m is related to T , m and V by the equation :

$$\text{Lindemann's Formula} \quad \nu_m = 3.08 \times 10^{12} \sqrt{\frac{T}{mV^{2/3}}}.$$

We give some figures for aluminium and silver.

	Calculated Frequency from Lindemann's Formula.	Observed from Specific Heats.	Frequency Calculated from Elastic Constants.
Aluminium .	8.3×10^{12}	8.3×10^{12}	8.0×10^{12}
Silver .	4.8×10^{12}	4.8×10^{12}	4.3×10^{12}

Without going into the details of the proof of Lindemann's formula, we observe that it connects together the following four magnitudes: (1) the maximum frequency ν_m , (2) the atomic weight, (3) the atomic volume, (4) the melting point. At the fusion temperature, the oscillations of the atoms, greatly increased in amplitude by the addition of heat, become of the same order of magnitude as the distances separating the atoms. The kinetic energy is given by $\frac{mv^2}{2}$, which introduces the atomic weight. The atomic distance involves the atomic volume. Lindemann's formula is obtained by equating the kinetic energy of the atoms at the fusion point, to the heat supplied, $\int C_v dT$ (where for C_v is substituted Einstein's expression for the specific heat).

Specific Heats of Monatomic and Polyatomic Gases Explained in Terms of the Quantum Theory. Rotation of the Molecule

The data given in the accompanying table represent experimental values.

Temperature in Degrees Centigrade.	Specific Heat of Hydrogen at Constant Volume.
— 240°	2.98
— 230°	3.00
— 190°	3.20
0	4.80
109°	4.83
500°	5.25
2,000°	6.55

For gases, as for solids, the specific heat shows a marked decrease at low temperatures. Hydrogen, for example, at 0° C. has a specific heat at constant volume $C_v = 4.80$, which is well below 5. Researches at very low temperatures in the neighbourhood of 30–50 degrees absolute have shown that all gases have specific heats approaching the value 3 appropriate to the

monatomic gases, and the inference is that all rotational motion of the molecules tends to cease at these low temperatures. Near the absolute zero, the rotational energy, which can vary in amount only by indivisible quanta, vanishes altogether.

We examine this point a little closer. The angular velocity of rotation (angle described per second) is $\omega = 2\pi\nu$. The kinetic energy for a body rotating about an axis with respect to which the moment of inertia has the value I , equals $\frac{1}{2} I\omega^2$, and according to the quantum theory,

$$\int 2T dt = nh.$$

In the actual case we have,

$$\int I \omega^2 dt = I \cdot 4\pi^2 \nu^2 \frac{1}{\nu} = nh$$

$$nh\nu = I + 4\pi^2\nu^2.$$

Thus,
$$\nu = \frac{hn}{4\pi^2I} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The number of complete rotations per second is therefore given by one, two, three . . . n times a well-defined constant, and intermediate angular velocities are impossible.

If the molecules of a monatomic gas (helium, neon, argon, mercury, zinc) do not exchange rotational energy when they collide, the explanation is not to be sought in the spherical form postulated in the classical kinetic theory. The reason is that their translational kinetic energy—which in a collision might be transformed into rotational energy—is insufficient to impart the *minimum* number of rotations per second demanded by the quantum theory. This minimum will depend on the largest moment of inertia I of the molecule, in accordance with equation (1)

$$\nu = \frac{h}{4\pi^2 \mathbf{I}}.$$

If the rotational energy $h\nu$ is very high, it may be inferred that the moment of inertia I is extremely small, that is to say, the matter is concentrated in a small volume, the atomic nucleus.

Thus for monatomic gases we can write down an inequality

expressing the fact that the energy of rotation $h\nu$ certainly exceeds twice the average kinetic energy of translation of a single molecule, which at ordinary temperatures equals for all gases 5.6×10^{-14} erg :

$$\frac{h^2}{4\pi^2 I} > 5.6 \times 10^{-14} \times 2.$$

Also, since for argon the specific heat retains the value 3 even at $3,000^\circ$ abs. at which temperature the average kinetic energy is ten times the value cited above, we may write,

$$\frac{h^2}{4\pi^2 I} > 10^{-12} \quad \text{and} \quad h\nu > \frac{1}{2} \cdot 10^{-12}.$$

The former of these two relations gives an indication of the magnitude of the moment of inertia, the latter sets a lower limit to the velocity of rotation.

The constant h has the value 6.55×10^{-27} . Hence the minimum number of rotations of the molecule per second is of the order 10^{14} and the moment of inertia of the argon atom is less than 10^{-42} . From the latter value we can determine the radius of the uniformly dense sphere which would have the same moment of inertia, and the same total mass, as the argon atom. The highly significant result of this calculation is that the diameter of the sphere measures only about one-hundredth the diameter of the atom derived from kinetic theory considerations. This means, as already pointed out, that the matter is located at the centre of the atom which must have an "openwork" structure, as we know to be the case from Rutherford's work. The nucleus is surrounded by a spherical *armature* almost without weight, which protects the atom from collisions and has the diameter which is observed in kinetic theory phenomena.

For polyatomic gases, in an analogous manner, it is possible to formulate the condition that at sufficiently low temperatures the molecules cease to rotate. Despite the fact that for polyatomic

gases the value of $h\nu = \frac{h^2}{4\pi^2 I}$ is smaller (and the colossal minimum angular velocity a little lower), it can still be laid down that $h\nu$ always exceeds double the kinetic energy of translation.

Cases in point are hydrogen and ammonia. It is possible (Perrin) to make a simple calculation fixing an approximate limit to the size of the hydrogen molecule.

We imagine the molecule to be made up of two spheres whose centres are a distance d apart. The masses of the two atoms are concentrated at their respective centres. The moment of inertia I of the system, with respect to an axis at right angles to the line of symmetry, is easily calculable. Having found I , the quantum of rotational energy $h\nu = \frac{h^2}{4\pi^2 I} \cong \frac{10^{-54}}{I}$, is determined, and we know this must exceed twice the mean energy of translation (5.6×10^{-15} erg) of a molecule of the gas, at a temperature in the neighbourhood of 30° abs. From this inequality an indication of the size of the molecule, the distance apart of the spheres, is obtained. It is found that this distance must be less than 1.2×10^{-8} cm., a value which agrees with the result 2×10^{-8} cm. furnished by kinetic theory for the diameter of the sphere of impact.*

It should be noted that the inequality of which we have spoken is in reality almost an equality, for above 30° absolute the specific heat of hydrogen shows at once a slight increase, as can be seen from the Table at the commencement of the paragraph. This rise implies the setting up of the rotational motion and, in the present case, we can argue that at about 30° abs. the rotational quantum $h\nu$ equals twice the average translational energy. This explains why the value found for the molecular diameter is nearly the right value.

To conclude, the specific heat of a polyatomic gas cannot correspond to any of the constant values predicted by the classical theory, $\frac{5}{2}R$, $\frac{7}{2}R$, etc., but must vary with the temperature. The value of C_v is the sum of contributions due to the energies of translation, rotation and vibration. Each of these is quantised. For example, the fact that from 25° to 50° abs. C_v for hydrogen

* The exact value deduced from the molecular spectrum is :
 0.75×10^{-8} cm. for the distance apart of the nuclei.
 5.67×10^{-41} gm. cm.² for the moment of inertia.

one of the possible wave-lengths. As $\lambda = \frac{1}{z}$ (z = number of waves in unit length) we shall have $r = \frac{2a}{\lambda} = 2az$.

This point lattice enables us to answer the question : how many oscillations are there in the cube, of wave number z lying between z and $(z + dz)$? Each point of the lattice in a spherical shell of radii r , $(r + dr)$ and of volume $\frac{1}{8} 4\pi r^2 dr$, represents one permissible value of λ . The number of lattice points in this layer will equal the number of unit cubes of which it is composed, in other words, its volume. Thus the number of vibrations is given by $\frac{1}{8} 4\pi r^2 dr = \frac{1}{8} 4\pi \cdot 4a^2 z^2 \cdot 2adz$, or

$$\text{total number of vibrations} = 4\pi a^3 z^2 dz.$$

For any closed volume θ , we shall have $4\pi\theta z^2 dz = 4\pi\lambda^{-4} d\lambda$ for the number of vibrations for polarised light, and $8\pi\lambda^{-4} d\lambda$, for ordinary light.

Every characteristic oscillation of the interior space can be regarded as an harmonic oscillator in which the magnetic energy corresponds to the kinetic energy of a mechanical oscillator, and the electrical, to the potential energy. According to the classical theory of equipartition, to every degree of freedom of a system in equilibrium there corresponds, on the average, the kinetic energy $\frac{1}{2}kT$. Hence to every oscillation considered here, average energy kT may be attributed, giving a total,

$$\Delta E = 8\pi\lambda^{-4} kT d\lambda.$$

Now

$$\Delta E = \frac{8\pi}{c} E_\lambda d\lambda,$$

and hence,

$$E_\lambda = c\lambda^{-4} kT$$

which is the Rayleigh-Jeans * formula referred to on p. 25.

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CHAPTER V

THE PHOTOELECTRIC EFFECT. THE REVERSE EFFECT. PHOTOELECTRIC CELLS AND THEIR APPLICATIONS

The Nature of the Photoelectric Effect

UNDER the influence of X-rays, ultra-violet light, and even visible light, a large number of metals and some gases emit electrons. This phenomenon is called the *photoelectric effect*.*

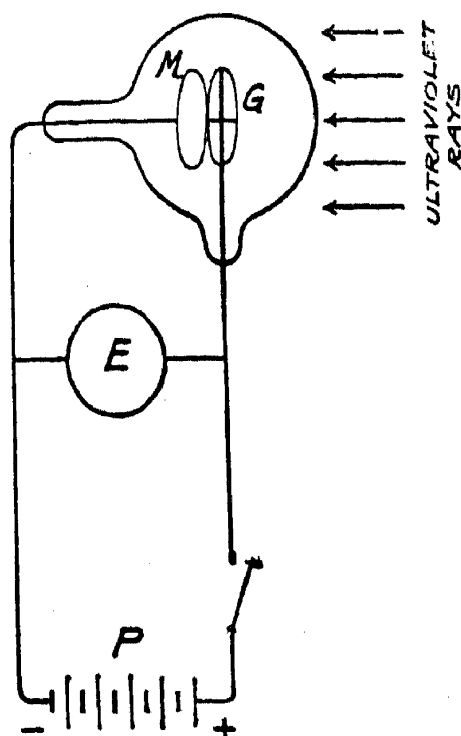


FIG. 35.

As regards the action of ultra-violet light, the metals may be arranged in order of increasing sensitivity, viz., zinc, magnesium, lithium, sodium, potassium and rubidium. In the case of potassium, and even more with rubidium, the emission of electrons takes place also under the action of visible light; certain sulphides (those of lead, antimony, silver, etc.) also exhibit the photoelectric effect.

The emission of electrons takes place immediately the light reaches the surface and ceases immediately the light is cut off. If the body is negatively electrified, it is discharged by the emission of the

* We shall not attempt to describe here the earlier work leading to the discovery and, later, the investigation of the photoelectric effect. As is well known, it was discovered by Hertz (1887) in one special case; Hallwachs was the first to investigate it directly (1888); there were then the experiments of Stoletow, Righi, Merritt and Stewarts; Lenard (1900) measured the velocity of the photoelectric particles. Merritt, Stewarts and Lenard himself suggested that these particles were the same as the particles forming the cathode rays, as is now known to be the case.

Elster and Geitel, from 1889 onwards, carried out very important and extensive researches which led directly to the construction and use of photo-cells for practical purposes.

electrons ; if it is neutral the photoelectric emission leaves it with a positive charge.

In order to demonstrate the phenomenon of the emission of negative electricity, due to the action of light, the apparatus shown diagrammatically in Fig. 35 may be used ; this is, in fact, a *photoelectric cell*.

This cell is the quick-acting and sensitive device used for the transmission of pictures, in astrophysics, and for many other purposes.

An evacuated quartz bulb, transparent to ultra-violet light, contains a plate M of the metal under investigation (*e.g.*, potassium, sodium, or zinc) and a large-mesh grid G, parallel to M. The two leads are connected to the electrometer E and then to the poles of the battery P. In this way the grid is raised to a potential of more than a hundred volts above that of the plate ; after the connection with the battery had been broken, it will be found that, when a beam of ultra-violet light falls on the metal, the electrometer indicates a fall in the difference of potential between G and M, owing to the escape of negative charges which are captured by the grid.

If, on the other hand, the sign of the potential difference between G and M be reversed, no such process takes place because in this case there is no emission of positive charges.

The number of electrons emitted per second by the action of a given monochromatic radiation is proportional to the intensity, increases rapidly with the frequency of the radiation, and is zero for all frequencies below a certain limiting value called the *photoelectric threshold*.

This limit depends on the chemical nature of the metal ; it is in the red for very oxidisable metals and in the ultra-violet for zinc, cadmium and mercury. For sodium the wave-length which produces the maximum effect is $\lambda_0 = 6,800 \text{ \AA}$. ; for lithium $\lambda_0 = 5,250 \text{ \AA}$. ; for mercury $\lambda_0 = 3,043 \text{ \AA}$.

The other fundamental rule is that the *initial velocity* with which the electrons leave the irradiated surface is quite independent of the intensity of the light producing the effect,* and depends

* P. Lenard, *Ann. der Physik*, 8, p. 149, 1902

solely on the frequency ; it has been found that the electrons expelled from a metal under the action of X-rays have a velocity which is similar to that of the electrons in the cathode stream which produced the X-rays themselves.

More exactly, the kinetic energy ($\frac{1}{2}mv^2$) of the electrons expelled from a metal which is irradiated in a vacuum by monochromatic radiation of frequency ν is given by the following equation due to Einstein :

$$\text{Einstein's equation} \quad \frac{1}{2}mv^2 = h\nu - \epsilon.$$

In other words, the kinetic energy of an electron leaving the surface is equal to the product of Planck's constant, and the frequency of the exciting radiation, less a quantity ϵ which is a *constant* for a given metal ; this quantity ϵ represents the work required to drag the electron out of the metal and is of the order of a few volts.*

To sum up the experimental facts so far stated concerning the photoelectric effect, we may say that :

(1) For incident light of a given spectral distribution, the *number* of photo-electrons emitted is proportional to the intensity of the light.

(2) The kinetic energy of the photo-electrons is a linear function of the frequency according to Einstein's formula :

$$\frac{1}{2}mv^2 = h\nu - \epsilon.$$

Hence every electron, apart from the quantity ϵ , which is interpreted as representing the work done in the process of removal from the body, is given an amount of energy proportional to the *frequency of the incident light* and independent of the nature of the substance.

(3) *The kinetic energy* $\frac{1}{2}mv^2$, when monochromatic light is used, is absolutely independent of the intensity of the light.

Important experiments,† in which the cloud method was used, have shown that the most probable direction for the expulsion of a photoelectron from an atom is close to the direction of the

* Atomic energies are usually expressed in volts : the number of volts is the potential difference necessary to give an electron the energy required to extract it from the metal.

† W. Bothe, *Zeits. für Physik*, 26, p. 59, 1924.

electric vector in the incident wave, but with an appreciable shift towards the direction in which the wave is travelling; the polar curve giving the intensity of emission (*i.e.*, the probability of emission) for the various directions therefore exhibits a maximum in a direction inclined slightly *forward* with respect to the wave-front (see Fig. 36); as the voltage on the tube producing the X-rays is increased, this displacement also increases.

The new mechanics explains these results completely and leads

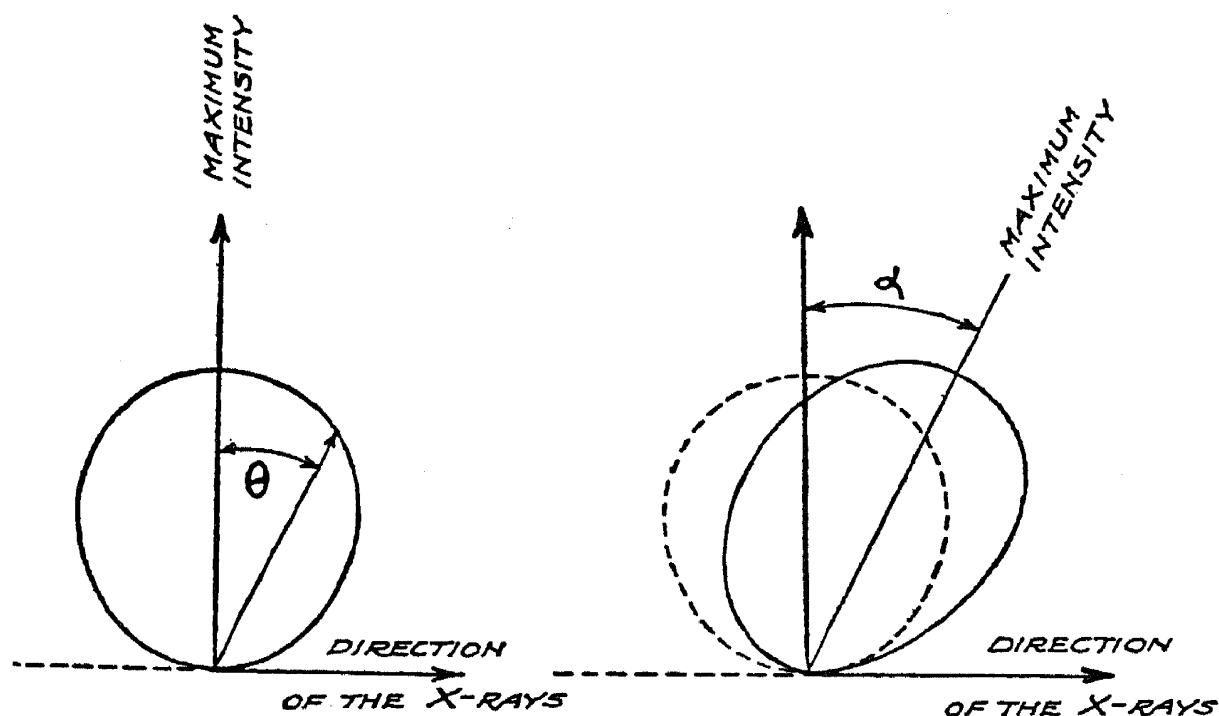


FIG. 36.

to the conclusion that the probability that an electron will be emitted in the direction θ is proportional to $\cos^2 \theta$.

The constant h is the same for all the metals and for all kinds of radiation; the best determinations of its value have been made in the case of the alkali metals, which emit electrons when illuminated with ordinary visible light, while the other metals require ultra-violet light; Millikan used sodium and lithium and obtained $h = 6.57 \times 10^{-27}$.

This constant is thus neither more nor less than Planck's constant!

When the light used is, for instance, in the violet where $\lambda = 0.4$ micron, the frequency is equal to $(3 \times 10^8)/(4 \times 10^{-7}) = \frac{3}{4} \times 10^{15}$, so that $h\nu = 5 \times 10^{-12}$ erg; this is the energy which a cathode

stream would have if the potential difference V between the electrodes were that given by the equation $eV = 5 \times 10^{-12}$, so that $V = 3 \times 10^8$ e.m.u., *i.e.*, 3 volts.*

This example shows clearly how, since ϵ is of the order of one or two volts, the expelled electrons—*i.e.*, the so-called photoelectrons—are left with an amount of energy corresponding to a fall of potential of one or two volts only.

If, however, the photoelectric effect is produced by means of X-rays or γ -rays, for which the frequency is much higher—*viz.*, of the order of 10^{18} to 10^{21} —the term ϵ becomes quite negligible compared with the energy $h\nu$, and the kinetic energy of the particle emitted by the atom when it is struck with a frequency ν is given by the simple relation $\frac{1}{2}mv^2 = h\nu$.

As shown in the example given above, the energy $\frac{1}{2}mv^2$ may be mentally connected with the difference of potential V necessary to obtain electrons of energy $\frac{1}{2}mv^2$ in a cathode stream, using the equation $\frac{1}{2}mv^2 = eV$; for this reason it is common to speak loosely of electrons of 1,000 volts, 2,000 volts, etc.

Those physicists who observed the photoelectric phenomenon were faced with a great difficulty from the very beginning; this was to find the reply to the following question: from what source does the electron acquire its kinetic energy when the distance from the light source is so increased that the intensity of the illumination is reduced practically to nothing although the velocity of the electrons shows no sign of diminution?

There must, evidently, be a kind of accumulation of luminous energy at the points from which the electrons are emitted, an accumulation which is inexplicable from the point of view of the uniform and isotropic propagation of electromagnetic energy; even if it be assumed that the light source only emits radiation discontinuously—like an occulting light—its propagation by waves spreading out isotropically in all directions would imply that it was extended more and more over successive spherical shells until these became so large that the illuminated metal could only receive an extremely small amount.

In fact, if it be calculated, on the basis of the wave theory,

* Remembering that $e = 1.59 \times 10^{-20}$ e.m.u.

how much energy a light source can radiate to an electron, the result is only a very small fraction of the energy which the electron actually receives; in fact—taking the example quoted by Millikan in his classical book—a standard “candle,” placed at three metres from a surface one square cm. in area, radiates to that area luminous energy equal to one erg per second; in the same interval of time, a body of the size of an atom—*i.e.*, having an area of the order of 10^{-15} sq. cm.—receives 10^{-15} erg. Now the energy $h\nu = \frac{1}{2}mv^2$, which an electron possesses when liberated by light, for which $\lambda = 0.5$ micron is 4×10^{-12} erg, *i.e.*, 4,000 times as much! If, then, it be considered that two-thirds of the energy of the white light emitted by a *standard candle* is in the form of radiation for which the frequency lies below that corresponding to $\lambda = 0.5$ micron (and is, therefore, incapable of affecting a surface of lithium or sodium, since these metals are only sensitive to this and higher frequencies), it will be seen that 4 hours must elapse before an atom of lithium or sodium can emit an electron.

Actually, however, such electrons are liberated immediately the light appears.

If the energy is not supplied externally, it can only be supposed that the electron already possesses such a store of energy that, at the time of the experiment, a very small additional amount will suffice to release it; it will then be emitted with an amount of energy equal to $h\nu$ where ν is the frequency of the *incident* radiation: what a mysterious mechanism this supposes for the atom, which must contain amounts of energy equal to $h\nu$ where ν may have any value!

The only plausible explanation of the facts seems to be the following, which is due to Einstein and to which we shall presently return in order to deal with it more fully: the energy emitted by a light source is always concentrated at certain points, not only in time but also in space; in other words, the light energy does not spread out uniformly in all directions, so becoming less and less intense; on the contrary, it always remains concentrated in the form of “light quants,” or grains, the magnitude of which depends solely on the *colour* and which are propagated in all directions with the velocity of light.

Each of these "light quants," when it reaches the metal, can give up its whole energy to one of the electrons within that metal, and this energy is naturally always the same whatever the distance from the light source. We can see that Newton's theory of emission is here revived in a modified form, the "particles" now becoming "grains" of energy.

Let us now return to Einstein's equation: $cV = \frac{1}{2}mv^2 = h\nu$.

If this equation be read from right to left it indicates what happens when corpuscular secondary cathode rays are produced by primary Röntgen rays, and it gives the maximum velocity of the electrons emitted from a substance which receives monochromatic radiation of frequency ν ; the same equation, when read from left to right, expresses the transformation of a corpuscular radiation composed of electrons having a velocity v and generating Röntgen rays of frequency ν when they impinge on the anticathode of an X-ray bulb.

This is the *reverse of the photoelectric phenomenon*.

Actually, as we know, the anticathode, when it is bombarded by electrons, emits a continuous spectrum having a lower limit equal to ν , *i.e.*, this emission stops abruptly at a frequency ν defined by Einstein's equation; this frequency is proportional to the potential applied to the electrodes of the X-ray bulb.

This, then, is the photoelectric effect; light waves fall on a metal surface and electrons are emitted with various velocities, some of them reaching a maximum value given by the equation

$$\frac{1}{2}mv^2 = h\nu - \epsilon,$$

this maximum being independent of the intensity of the incident light. This is a paradoxical result.

If the process be analysed in the light of the classical ideas so firmly established during the last century, it must be imagined that the electromagnetic waves excite the electrons in the metal so as to cause them to execute forced oscillations; these become gradually greater and greater in amplitude until the electron leaves its place altogether and comes away from the metal.

Anyone would confidently predict that the greater the intensity of the light, the greater would be the residual energy E retained

by the electron after overcoming the forces opposing its release, yet actually E is independent of the intensity of the incident light.

The maximum energy of the electrons released by radiation of frequency ν is equal to the quantity $h\nu$ (which is always the same whatever be the metal illuminated, since it is characteristic of the light and not of the metal) less a quantity ϵ , which is the quantity of energy given up by the electron in traversing the external layer of the metal. Everything occurs just as if each electron received an amount of energy $h\nu$ from the light, as if this energy were concentrated in small packets or particles (light quanta) and one

The Photoelectric Effect and the Reverse Effect

Radiation.	Frequency per sec. ν .	Wave-length in cm. λ .	V in volts $V = \frac{h\nu}{e}$.	Velocity of the Electrons $v = \sqrt{\frac{2eV}{m}}$.
Yellow light .	5×10^{14}	6×10^{-5}	2	8×10^7
Ultra-violet .	3×10^{15}	10^{-5}	12	2×10^8
X-rays .	3×10^{18}	10^{-8}	12,000	6×10^9
γ -rays .	order of 10^{21}	order of 10^{-11}	1 million and over	mass varies with velocity

of these, *only one*, were taken up by an electron. It is to be noticed that the value of the constant h is identical with that which occurred in Planck's theory and which has already been given by Planck himself.

As mentioned above, it will be seen that this class of phenomena revives, in a way, Newton's idea that light is propagated by the emission of corpuscles; on the strength of Newton's influence this theory triumphed for a long time, and it was not displaced until the nineteenth century by the influence of Fresnel and Young, who demonstrated the undulatory character of light by means of the phenomena of interference and polarisation.

Any return to the old theory would seem to be impossible, and yet the last twenty years have brought to light a group of phenomena in which there is something kinetic in the undulatory

radiation and something periodic in the passage of corpuscles. This will be seen more clearly later on.

In the table on p. 169 we give figures which will fix the order of magnitude of the quantities which appear in the photoelectric phenomenon and its reverse. Wave-lengths are expressed practically in Ångströms ($1 \text{ Å} = 10^{-8} \text{ cm.}$), potential differences in volts, electron velocities in cm. per second.

Starting from the low frequencies, we find first of all the electric oscillations for which the quantum of energy $h\nu$ is very small; electric waves of 300 metres have a frequency of 10^6 , so that :

$$V = h\nu/e = (h/e) (c/\lambda) \quad (c = \text{velocity of light} = 3 \times 10^{10} \text{ cm./sec.})$$

and the corresponding potential difference is very small, viz., 4×10^{-9} volts; yellow light has a frequency of 5×10^{14} , corresponding to a quantum of the order of 2 volts,* and this is comparable to contact differences of potential, i.e., to the differences of electric potential which exist between metallic surfaces in contact. This fact is the cause of a great deal of difficulty in experiments on photoelectric phenomena.

As we go up the scale in the direction of increasing frequency, the ultra-violet rays begin to have a larger quantum; in the case of the Lyman rays, which lie beyond the ultra-violet, V equals 10 to 20 volts.

The photoelectric effect, it must be remembered, can be produced in gases and vapours as well as in metals; in order that the atom may be ionised by the action of the light the quantum ($h\nu$) of the latter must exceed the energy of ionisation W_0 ; thus $h\nu_0 = W_0$ gives the value of the limiting frequency which can produce ionisation, the frequency which has been called the photoelectric threshold.

If the incident light has a higher frequency the difference ($h\nu - W_0$) is the energy of the electron released from the atom.

Millikan's Verification of Einstein's Equation

It has already been said that Einstein, in 1905, in order to connect the photoelectric phenomenon with the results obtained

* This is an incorrect method of expression, but it is commonly used.

by Planck in Berlin in his studies of black-body radiation, proposed the equation $\frac{1}{2}mv^2 = Ve = h\nu - \epsilon$.

This equation states that the energy of an electron leaving the surface of a metal receiving light of frequency ν is equal to $h\nu - \epsilon$; the measure of this energy is the product Ve , where V is the potential difference which must be applied to the electrode in order to prevent the electron from leaving it.

At that time, as Millikan pointed out, it was not known how this potential which had to be applied to stop the emission of the electrons would vary with the frequency of the monochromatic light, nor, on the other hand, how the constant h , the numerical value of which had been given by Planck, could be related to photoelectric emission.

After ten years of research, however, Einstein's equation, the intuitive product of genius and at that time lacking any experimental basis, was found to agree perfectly with the facts.

Millikan (1916) made use of apparatus which, as it was complicated and had to be placed in a vacuum chamber, he jestingly called "a machine-shop in vacuo." In order to verify the simple relation $Ve = h\nu - \epsilon$, it was necessary to make experiments on a number of different frequencies; on account of the sensitivity of the alkali metals to ordinary light (frequencies appropriate to the red and to the violet), Millikan employed these metals and, as they oxidise very readily, he carried out his experiments in a vacuum. Cylinders of these metals were placed on a disc and fresh surfaces were obtained by scraping them while inside the apparatus; this was achieved by means of a special device actuated by an electromagnet (Fig. 37). The fresh surface so obtained was then illuminated with a beam of monochromatic light provided by a spectroscope; the energy of the liberated electrons was measured by raising the emitting

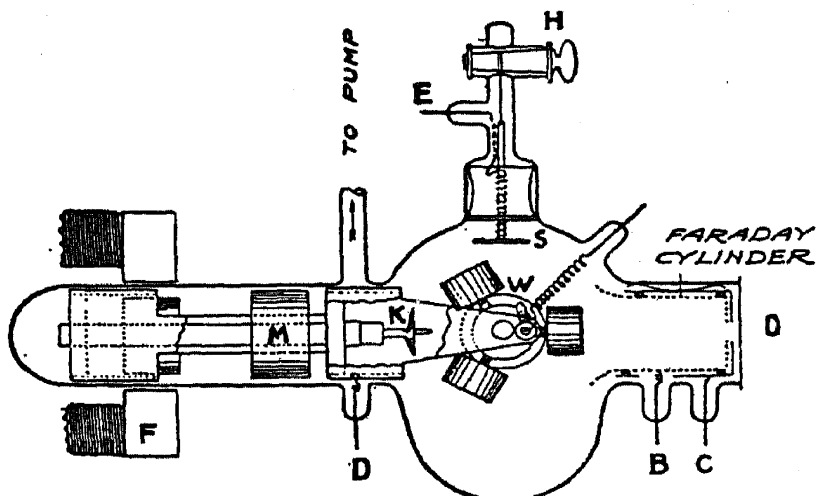


FIG. 37.

surface to a positive potential just sufficient to prevent any of these electrons from reaching a cylinder of metal gauze placed opposite the illuminated surface; this cylinder was connected to an electrometer and so acted as a detector of any electronic charges that might reach it.

From the equation $Ve = h\nu - \epsilon$ we derive $\Delta V \cdot e = h\Delta\nu$ or $h = e (\Delta V/\Delta\nu)$, and thus, if h is really a constant, the curve connecting the observed volts with the frequency ν should be a straight line, having a gradient equal to h (see Fig. 38).

This is precisely what Millikan found, and he deduced, from

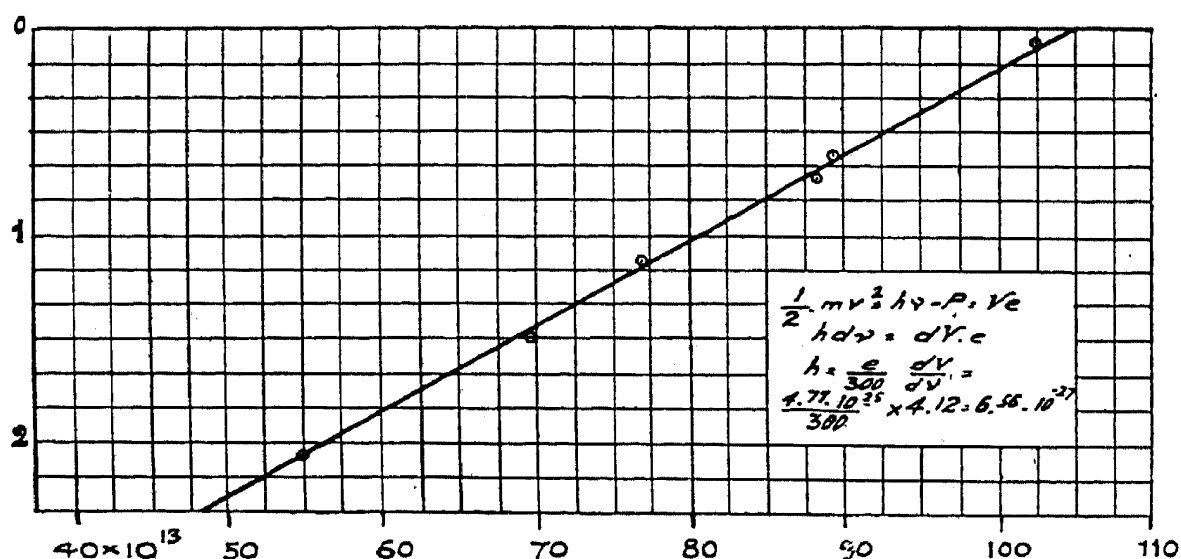


FIG. 38.

a series of important researches on this subject, the value $h = 6.56 \times 10^{-27}$.

With regard to the apparatus used by Millikan, we ought to remark that, since the metal emitting the electrons is different from that used for the Faraday cylinder which picks them up, it is necessary to *take account of the contact potential difference* K (of the Volta effect) between this cylinder and the metal being investigated, so that the actual equation representing what takes place is as follows :

$$\frac{1}{2}mv^2 = (P + K)e = h\nu - w = h\nu - h\nu_0$$

P represents the potential necessary to stop the electrons; the difference of potential is measured directly between the disc of metal under investigation and a test plate S , which is of the same

material as the Faraday cylinder, and has a similarly treated surface.

Blocks of the three metals sodium, potassium and lithium are placed on the periphery of the wheel W, which is caused to rotate by means of an electromagnet not shown in the figure. The electromagnet F controls the rotary knife K which serves to scrape the surfaces of the sample to be investigated; the beam of monochromatic light which liberates the electrons enters the apparatus at O. Millikan measured a number of photoelectric currents to determine what was the value of the potential corresponding to zero current (see Fig. 39). Before doing this it was necessary to bring the alkali metal into contact with the test

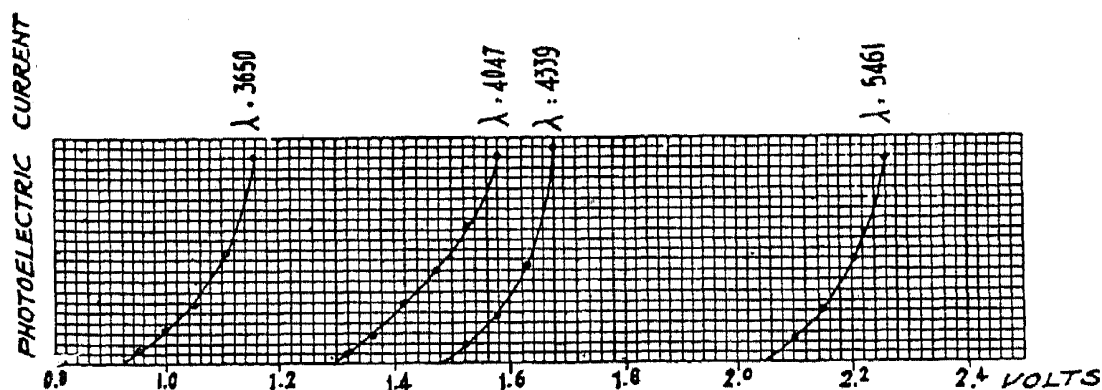


FIG. 39.

plate S, and since the difference of potential between this plate and the metal could be measured (since it was the same as that between the metal and the Faraday cylinder), Millikan was able to verify the validity of the equation

$$(P + K)e = h\nu - h\nu_0$$

For a direct measurement of the contact potential K, Millikan made use of Kelvin's potentiometer method, *i.e.*, he measured the potential which had to be applied to one of the two metals in order to *compensate* for the Volta effect, after S had been removed from contact with the metal under examination.

The work just described gave, too, an exact figure for Planck's constant h , and in this connection we may remark that the existence of the e.m.f. K did not introduce any error, since, from the equation $(P + K)e = h\nu - h\nu_0$, in which K and ν_0 are constants,

it follows that $e \cdot dP = h \cdot d\nu$ so that $h = (dP/d\nu)e$; thus, from the slope of the straight line in the graph connecting P and ν , Millikan immediately deduced the value of h , as has been said already.

Actually, however, since K was not constant, on account of the variable effect of the surface of copper oxide in the collecting cylinder, it was necessary to make a simultaneous measurement of the contact potential, or at least to ensure that the conditions were so maintained that K remained constant during the measurement of the photoelectric currents. It was from the way in which these currents changed with change of the opposing potential (see Fig. 39) that Millikan deduced the value of the potential P which corresponded to zero emission; by repeating these measurements of photoelectric currents for various values of λ he obtained the relation between dP and $d\nu$.

The Limit of the Continuous Background given by an Anticathode Bombarded by Corpuscular Radiation and the Determination of the Quantum h . Duane and Hunt *

We know already, from what has been stated with regard to X-rays, that if an incandescent cathode X-ray tube be excited and caused to operate under a constant potential V , the electrons reach the cathode with energy $eV = \frac{1}{2}mv^2$. This energy may be varied at will by adjusting V .

The radiation emitted from the anticathode may be analysed by means of a spectrometer furnished with an ionisation chamber, so that the rays reflected from a crystal at different angles may be examined while the crystal remains fixed in position with respect to the incident radiation. If the ionisation intensities be then plotted against wave-lengths for a voltage V_1 a curve is obtained; similar curves can be found for other voltages $V_2, V_3, V_4 \dots$ these start abruptly on the left (*i.e.*, the short wave-length end), rise to a maximum and then fall more slowly as λ increases (see Fig. 40).

It will be noticed that the starting points shift continually towards the higher wave-lengths; as the potential rises, the same

* Duane and Hunt, *Phys. Rev.*, Vol. 6, p. 166, 1915.

thing happens with the *maxima*; for a given potential there are no rays which have less than a certain limiting wave-length which is the *limit of the continuous spectrum*.

These curves bear a superficial resemblance to the family of curves showing the spectral energy distribution of the black body, but there is no connection between the latter phenomenon and the energy emission from an anticathode; further, it should be remembered that the curves in the diagram cannot show the real intensities of the radiations, but only give the ionisations produced by the X-rays; these provide just a rough indication, not a true measure, of the energy.

It is possible—by means of the spectrometer—to construct another interesting diagram showing the effect, at any given wave-length, of varying the voltage on the X-ray tube; the spectrometer is kept fixed and the isochromatic curves—curves for the same colour—are then obtained (see Fig. 78, Vol. I). We have already dealt with the subject in Chap. VI of Vol. I.

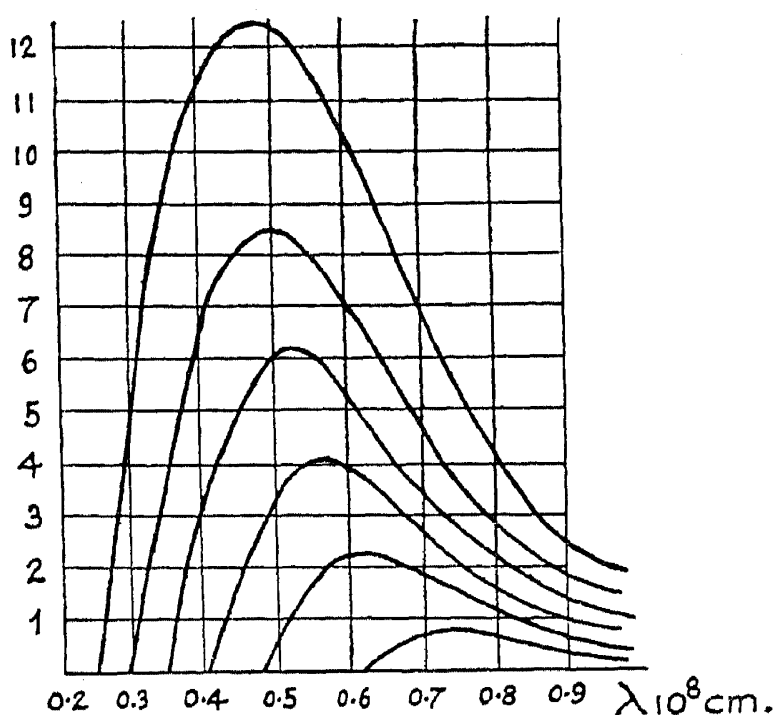


FIG. 40.

Either method of representing the results leads to the same conclusion, *i.e.*, that the intensity of the X-radiation produced becomes zero for a voltage V , the value of which is connected with the limiting frequency (below which no radiation is produced) by the fundamental relationship: $h\nu = eV$.

In short, the values at the bases of the curves in the figure satisfy the equations: $h\nu_1 = eV_1$, $h\nu_2 = eV_2$, $h\nu_3 = eV_3$, etc., and it is found that h is absolutely constant. By tracing the curves of Fig. 78, Vol. I, and continuing them until they intersect the axis of abscissæ, the value of h may be found very exactly since e , ν and V are known.

A number of workers have undertaken this determination, using the method just indicated ; we may quote the following among the best-known results :

Duane and Hunt (1915) found 6.51×10^{-27} erg sec.

Blake and Duane (1917) found 6.55×10^{-27} erg sec.

Wagner (1918) found 6.53×10^{-27} erg sec.

The value now taken as the most probable is 6.545×10^{-27} erg sec.

The Experiment of Maurice de Broglie and Ellis on the Magnetic Spectra of Corpuscular Radiations. Determinations of the Energy Levels of the Atom *

It must be remembered that a metal bombarded by X-rays emits characteristic secondary radiations of two kinds, *i.e.*,

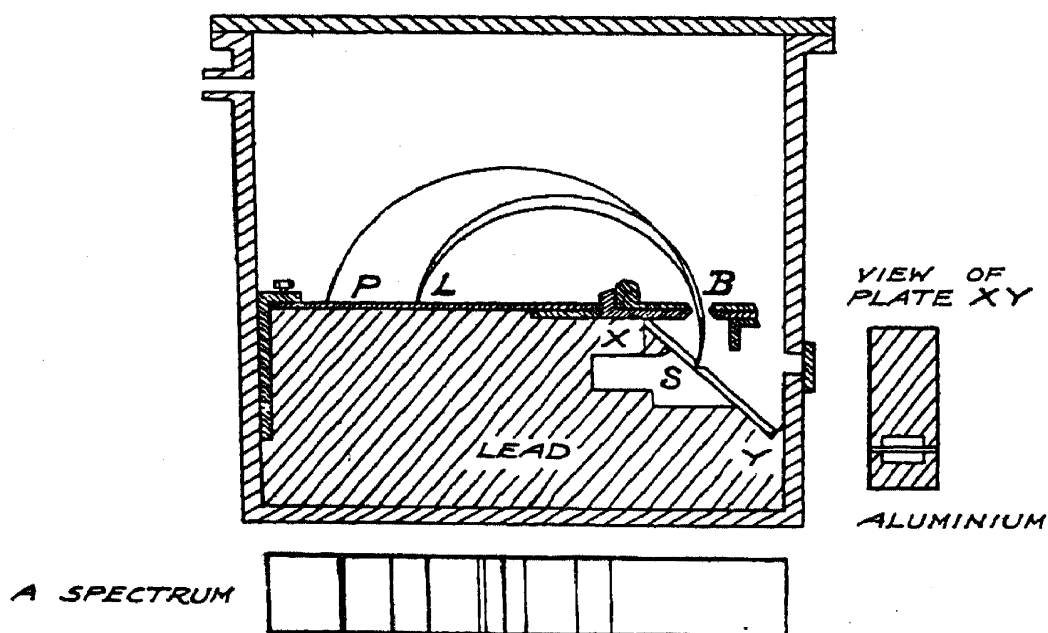


FIG. 41.

corpuscular and periodic ; the latter are X-rays—the so-called fluorescent radiation—which are not deflected by a magnetic field ; the former, on the other hand, are composed of *electrons* which describe a circle, if they move in a uniform magnetic field.

The electrons shot off from a radiator irradiated by X-rays do not all move with the same velocity, but there are bundles of electrons, and in each bundle the kinetic energy of each electron is given by $h\nu - \epsilon$.

* Other names associated with this work are Kang Fuh Hu, Lewis, Simon, Whiddington and H. Robinson.

Actually, the kinetic energy of an electron is equal to the energy $h\nu$ diminished by the work needed to extract the electron, there are different energy levels corresponding to the various electrons in the atom of the radiator ; hence the various elementary energies coming from different levels cannot all possess the same kinetic energy. De Broglie was interested in the verification of this law and in demonstrating its correctness to those who—a few years before—had affirmed that the energy of the emitted particles was $h\nu$.

The experiment was carried out with the apparatus shown in Fig. 41.*

The apparatus is enclosed in a small bronze box in which a vacuum is maintained ; an external magnetic field acts normally to the plane of the paper : S is the radiator in the form of a thin slit ; P is a photographic plate ; B a narrow window. The muscular radiation, composed of electrons, instead of issuing in a straight line and passing through the window, is bent round in a circle by the action of the magnetic field, H, and strikes the photographic plate at P or at L. The radius of the circle is $R = mv/He$; it might seem that the different arcs, corresponding to the various directions, would not all strike the plate at the same point P ; but it is easy to see that if the window is very narrow—that it can be regarded practically as a point—the various arcs, since they pass through the same two fixed points B and S, have the same radius $R = mv/He$, must also all pass through the same point P, approximately.

In practice R is of the order of 12 centimetres. For any given frequency of radiation acting on the secondary radiator, there are many lines on the photographic plate as there are energy levels ; this provides a means for analysing the energy levels and, consequently, for finding all the terms ϵ appearing in the equations :

$$\frac{1}{2}mv_1^2 = h\nu - \epsilon_1 \quad \frac{1}{2}mv_2^2 = h\nu - \epsilon_2, \quad \text{etc.}$$

- * M. de Broglie, *Journ. de Physique*, 2, p. 265, 1921.
 R. Whiddington, *Phil. Mag.*, 43, p. 1116, 1922.
 H. Robinson, *Roy. Soc., Proc.*, 104, p. 455, 1923.
 L. Meitner, *Zeits. f. Physik*, 11, p. 35, 1922.
 J. Thibaud, *Comptes Rendus*, 178, p. 1706, 1924.

A monochromatic primary radiation gives, in fact, a corpuscular spectrum, which is the analysis of the energy levels in the atom irradiated. Conversely, if attention be confined to a single level, the corpuscular spectrum corresponding to the various frequencies of the primary radiation will give an analysis of this radiation, *i.e.*, the spectral composition of the primary X-rays.

This is a method which can be used instead of the crystal method for the analysis of X-rays; the metals used as radiators are zinc, molybdenum, tin, lead, barium, copper, gold and many others. For the stimulating X-radiation the rays given by tungsten, for example, are used. It is customary to speak of the K line of silver excited by the $K\alpha_1$ line of tungsten, by the $K\alpha_2$ line of tungsten, etc.

When the energy of the emitted corpuscles is raised by using γ -rays for excitation, it is no longer possible to identify this energy with $\frac{1}{2}m_0v^2$, where m_0 is the stationary mass of the electron; instead it is necessary to use the value indicated on the theory of relativity, viz.

$$\text{kinetic energy} = m_0c^2 \left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right)$$

and thus the experiment on magnetic spectra confirms the relativity formula.

A large number of investigations of these corpuscular spectra have been made with γ -rays for various purposes, *e.g.*, to compare the spectra produced by isotopic elements, or to deduce from the lines obtained the frequencies of the γ -rays where these are too great to be measured by means of crystals.

***The Magnetic Spectra produced by γ -rays and the Measurement of the Wave-lengths of these Rays**

We shall now see an important application of the photoelectric effect in the determination of the wave-lengths of γ -rays.

Direct measurements of the wave-lengths of γ -rays have been made by means of crystals; this method is, however, of limited application on account of the smallness of λ ; an indirect method of analysis developed later, however, is based on the *magnetic*

spectrum produced by the electrons expelled from an atom by γ -rays and also that given by the *primary* β -rays which accompany the γ -rays.

We have already shown how Robinson and others have succeeded in analysing the spectra produced photoelectrically by means of X-rays of known frequency acting at the different energy levels in the atom. The converse of their procedure was employed by Ellis *; knowing the energy levels W_1, W_2, W_3 , he could determine the frequency of the γ -rays by using the fundamental formula :

$$\text{kinetic energy } L_1 = h\nu - W_1,$$

in which L_1, L_2, L_3 are known, allowing for the fact that, as stated already, L is not simply given by $\frac{1}{2}mv^2$, but by the relativity formula :

$$L = m_0c^2 \left(\frac{1}{\sqrt{1 - v^2/c^2}} - 1 \right).$$

Ellis used apparatus similar to that shown in Fig. 41, taking radium C as his source of γ -rays and lead, platinum or tungsten as the source of electrons. He was thus able to find the velocity v and therefore L , since the magnetic field and the radius of the trajectory were known.

The highest frequency reached with γ -rays is 5.4×10^{20} ; the corresponding quantum is 3.54×10^{-6} erg. This frequency is 20 times as great as that of the most penetrating X-rays, so that the quantum is also 20 times as great and can remove the most firmly bound electron from the heaviest atom. These γ -rays are emitted from the nucleus of radium C as it changes to radium C'.

In later researches the metal which radiates the photoelectrons has been eliminated, and the experiment in which the magnetic spectrum is used to determine the frequencies of the γ -rays is carried out as follows :

Since one frequency gives rise to a group of lines, several frequencies will give rise to a large number of lines ; it therefore becomes a matter of finding, by a process of trial and error, what are the frequencies which furnish a complete explanation of the

* C. D. Ellis, *Roy. Soc. Proc.*, 99, p. 261, 1921.

lines actually observed, the energy levels from which the β -electrons are emitted being known ; the kinetic energies, L , and the amounts of work, W , done in extracting the electrons are known so that it is necessary to find the frequencies ν_1, ν_2, ν_3 , etc., which explain the largest number of lines in accordance with the equations $L_1 = h\nu_1 - W_1, L_2 = h\nu_2 - W_2$, etc. For instance, Meitner and Hahn have succeeded in separating 49 lines given by the β -rays from radioactinium ; of these, 37 can be ascribed to the action of 12 species of γ -rays on 9 classes of electrons.*

*The Energy Levels of the Radioactive Nucleus Measured by Means of γ -rays

The measurements of Ellis and Skinner† on γ -rays (emitted from radium B and C) and Black's measurements‡ on the γ -rays emitted from thorium, have led to the important discovery that there are energy levels within the nucleus and that the passage of an electron from one level to another gives rise to γ -rays in the same way as the X-rays are caused by transfers of electrons from one extranuclear level to another inside the atom. What occurs is thought of as taking place thus : we know that from the frequencies we can find the energy levels, W , since $W_1 - W_2 = h\nu_1$, hence, when certain levels have been deduced, these must give rise naturally to the frequencies actually observed for other γ -rays.

By following this process, Ellis and Skinner have been able to postulate a series of *seven energy levels* for the nucleus of radium B, these seven levels giving rise to *fourteen* lines ; some of these correspond to frequencies which have already been measured directly by the crystal method (by Rutherford and Andrade).

The following are the values of the seven levels :

A = 0	B = 0.537×10^5 volts.
C = 0.625×10^5 volts.	D = 2.572×10^5 volts.
E = 2.942×10^5 volts.	F = 4.048×10^5 volts.
G = 5.31×10^5 volts.	

* See the work of L. Meitner, *Zeits. f. Physik*, 9, p. 131, 1922 ; 11, p. 35, 1922 ; 19, p. 307, 1923 ; 23, p. 169, 1924.

† *Roy. Soc. Proc.*, 105, pp. 165, 185, 1924.

‡ *Roy. Soc. Proc.*, 106, p. 632, 1924 ; 109, p. 166, 1925.

From the combinations $B \rightarrow C$, $A \rightarrow B$, $A \rightarrow C$, $F \rightarrow G$, etc., the following fourteen lines are produced :—

$B \rightarrow C$	1.37 Ång.	$B \rightarrow E$	0.051 Ång.
$A \rightarrow B$	0.230 „	$A \rightarrow B$	0.048 „
$A \rightarrow C$	0.196 „	$D \rightarrow G$	0.045 „
$E \rightarrow F$	0.115 „	$A \rightarrow F$	0.042 „
$F \rightarrow G$	0.099 „	$B \rightarrow F$	0.035 „
$C \rightarrow D$	0.067 „	$C \rightarrow G$	0.0265 „
$B \rightarrow D$	0.061 „	$B \rightarrow G$	0.0255 „

Fig. 42 gives a concrete idea of the system of levels and the corresponding lines.

These researches are of the greatest importance, since they show that the nucleus possesses a structure which is subject to quantic

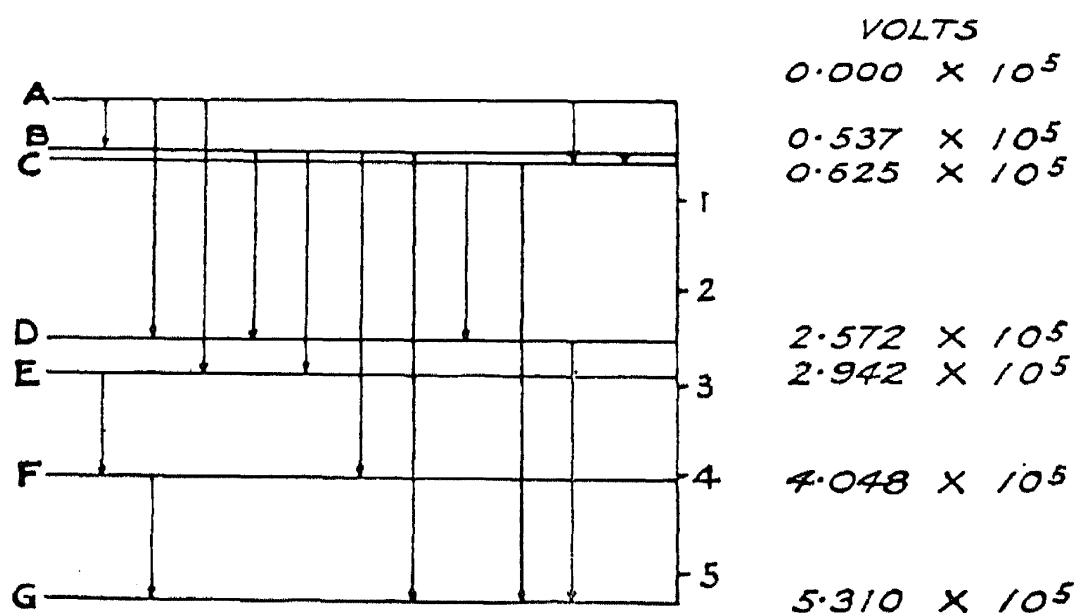


FIG. 42.—Energy levels of the nucleus of radium B.

rules ; we shall see in Chap. VIII how the new mechanics has succeeded in applying its statistical methods to this structure and in calculating the “*average life*” of the nucleus, *i.e.*, the probability of the phenomenon of radioactive disintegration of an atom, and even in predicting the energy of the α -particle emitted from the nucleus.

Various Determinations of Planck's Constant h *

Now that we have (on p. 171) described yet another method for determining the constant h which at the present time dominates the whole of the new physics, we may make a summary of the methods so far described.

(1) In considering black-body radiation, starting from the two values of Wien's and Stefan's constants which are known with fair precision, we have shown that the value obtained is 6.55×10^{-27} .†

(2) Spectroscopic data give the value of the constant ν_0 which occurs in the Balmer series, and from this constant, which is $2\pi^2me^4/h^3 = 3.29 \times 10^{15}$, the value of h may be obtained. It is found that $h = 6.547 \times 10^{-27}$.

(3) From the specific heats of the elements at low temperatures, as given by the experiments of Keesom and Kammerlingh-Onnes already described, it is possible to deduce h which occurs in the expression for the energy involved and therefore also in the expression for the specific heat; the value of h found is 6.59×10^{-27} .

(4) From the photoelectric effect in the cases of sodium and lithium, Millikan (1914 and 1915) found the values 6.56 and 6.58×10^{-27} .

(5) Blake and Duane (1917), using X-ray spectra and the fact that there is a limiting frequency corresponding to any given potential across the tube, obtained from the equation $h\nu = Ve$ the value $h = 6.555 \times 10^{-27}$.

The state of affairs thus indicated is very satisfactory; quite

* A complete account of this matter will be found in the *Handbuch der Physik*, Vol. XXIII, p. 279, article by R. Ladenburg.

† It is possible to start from the relation, found on p. 17, connecting the temperature T with the wave-length λ_m corresponding to the maximum point of the curve $E = f(\lambda T)$ for the black body. It has been seen, in fact, that

$$\frac{N}{R} \frac{hc}{\lambda_m T} = 4.965, \text{ i.e., } \lambda_m T = b = \frac{ch}{k \times 4.965}$$

where b is Wien's constant; from a study of the isothermal curves, λ_m is found for the spectrum of the black body at temperature T , and hence b is known so that h is calculable.

Alternatively, it is possible to use the relation found on p. 28 :

$$h^3 N^4 = 21.56 \times 10^{11} \times (1/\sigma)$$

where σ is Stefan's constant and N is Avogadro's number. The value of σ is found experimentally by measuring the total energy emitted by a black body and using the formula $Q = \sigma T^4$.

different phenomena, having no apparent connection with each other, give the same value for this mysterious constant of the quantum theory. We shall see it reappear in magnetism and in the Compton effect, where other phenomena provide still further means of determining it. The value adopted as the most probable at the present time is 6.545×10^{-27} .

Light Quanta

It has been seen that the emission of electrons takes place as if the energy of the incident light were concentrated in bundles, or light quanta, or corpuscles, and as if one of these were assigned to each electron.

Further, the production of radiation by the sudden stoppage of a rapidly moving electron when it collides with a metal, takes place as if the energy of the radiation were actually concentrated in units equal to $h\nu$ and as if one of these units were produced by the whole of the energy given up on the stoppage of an electron. These two complementary rules summarise the fact that, if certain electrons act on an anticathode so as to cause it to emit characteristic radiations, and if those radiations which have the highest frequency fall on a metal they cause it to emit electrons which have the same velocity as the primary electrons.

The part played by the constant h in the photoelectric phenomenon and its converse is a very striking result, but we shall now describe a further result which has not been met with in our work so far.

When high speed electrons move through vaporised mercury, lithium or magnesium, as long as energy of the electrons is less than a certain value, no light is emitted, but above this point there are series of energy values which can excite the atom and cause it to radiate; for instance, one line has a wave-length of 2,536 Ångström in the case of mercury, 5,890 Å. for sodium, and 4,571 Å. for magnesium.*

Here, again, as in the case of X-rays, the appearance of the

When a vapour is continuously excited by a self-maintained spark discharge, the atoms emit a large number of different radiations forming a complicated spectrum very rich in lines; if, however, the energy of the

line takes place suddenly and, in the case of mercury, the line mentioned appears when the bombarding electrons have a velocity of exactly 4.9 volts. From the equation $Ve = h\nu$, the frequency can be obtained at once and, remembering that 1 volt = 1/300 absolute units, it is seen that

$$(4.9 \text{ e}/300) \div (c/\lambda) = 6.55 \times 10^{-27}$$

since $\lambda = c/\nu$. This gives $\lambda = 2,536$ Ångström.

Hence the stimulation of the radiation constituting one line of the spectrum, owing to the collision of an electron with an atom, occurs exactly as if the energy of the radiation were concentrated in units equal to $h\nu$, for such quanta are actually taken, one by one, from the electrons and transferred to an atom.

These three phenomena which have been briefly described—viz., the excitation of gases or vapours, the photoelectric effect and its converse—thus agree in indicating the existence of light quanta; everything takes place as if the energy were actually concentrated in particles or quanta or bundles equal to $h\nu$ and as if each of these were individually created or destroyed during the process of emission or absorption.

Even this is not all, however; during the year 1923 the young physicist, Arthur Compton, then at the University of Washington, discovered another phenomenon which formed the best possible proof of the hypothesis of light quanta put forward by Einstein, a proof which gave a complete picture of the effect of the reaction between quanta of radiation and electrons; in his honour this phenomenon is called the *Compton Effect*. It shows conclusively that a light quant, when it meets an electron, really behaves like a particle which, as it strikes another particle obliquely, is deflected from its path and also changes the numerical value of its velocity so as to obey the laws of collision between elastic bodies, viz., those laws which express both the conservation of kinetic energy and the conservation of momentum. We shall see this in detail in Chap. VI.

bombarding electrons is controlled in the manner described above, so that it is equal to the value given by

$$\frac{1}{2}mv^2 = Ve = h\nu$$

then only one line of the spectrum is produced.

The Compound Photoelectric Effect

C. T. R. Wilson * and P. Auger † observed, in their photographs of *expansion clouds*, that when X-rays expelled photoelectrons from heavy atoms, it often happened that two or more electrons were expelled simultaneously from the same atom. Auger deduced from the paths of such electrons that, when this phenomenon occurred, the energy of the electrons was not greater than that of the light quant incident. When two electrons are expelled at the same time in a single elementary action, the energy of an electron is

$$\frac{1}{2} mv^2 = E = h\nu - h\nu_K \quad . \quad . \quad . \quad . \quad . \quad (1)$$

which indicates that the kinetic energy is equal to the energy of the light quant less the work required for extraction from the K energy-level; but the second electron possesses energy given by

$$\frac{1}{2} mv_1^2 = E_1 = h\nu_k - 2h\nu_L$$

where ν_L is the frequency corresponding to energy-level L. Now since the energy liberated in passing from the level L to the inner level K is $h\nu_K - h\nu_L$, equation (2) shows that a transformation has taken place inside the atom, an electron having passed from the state L to the state K where a place has been left free by the other electron; thus the energy $h\nu_k - h\nu_K$ has changed directly into the corpuscular form without having passed through the form of electromagnetic radiation.

This is the Auger effect. Expressed in words, it comes to this: The effect of X-radiation on an atom of a body is to remove an internal electron, and the place thus rendered vacant is filled by an electron belonging to a higher quantic group; the energy thus set free may be transformed into a light quant, and in this case secondary (or fluorescent) Röntgen radiation is emitted; it may, however, happen that another electron is set free, and in that case it leaves the atom with a kinetic energy equal to the difference between the amount of energy liberated and the energy which binds it to the atom.

* *Roy. Soc. Proc.*, 104, p. 1, 1923.

† *Journal de Physique*, 6, p. 205, 1925.

Photoelectric Conductivity of Solids

The photoelectric effect so far considered is a surface effect, but the absorption of quanta of radiant energy may also cause a volume emission of electrons if the radiation is capable of penetrating into the interior of the body.

This liberation of electrons inside a dielectric or a body with a high resistance results in an increase of specific inductive capacity and of conductivity. This effect has been noticed in rock salt, fluorite, quartz, paraffin, etc., when these are exposed to X-rays. For instance, the electrical conductivity of sulphur may be increased 100 times.* These internal effects are actually very complicated and difficult to interpret; Gudden and Pohl, in experiments on crystals of diamond and zinc blende (1920), have succeeded, by taking special precautions, in separating the direct effect of the absorption of the energy falling on the substance from the secondary effects due to the displacement of charges within the crystal, and in this way they have made a true measurement of the former quantity. Gudden and Pohl were thus able to show that the number of electrons liberated inside the crystal was exactly equal to the number of quanta absorbed and, from the numerical results obtained, they were able to deduce an approximate value for Planck's constant. They found

$$h = 6.8 \times 10^{-27} \text{ erg sec.}$$

All the crystals which exhibit the phenomenon of photoelectric conductivity have a very high refractive index.

The most important property, from the point of view of practical application, is that exhibited by thallium sulphide. This substance changes in specific resistance under the action of light and also of infra-red rays. These variations of resistivity are made use of in the thallium sulphide "resistance cell," which may be used as a detector for light signals in photo-telephony and as an instrument for measuring radiant energy in photometers and "illuminometers" in which such cells are used in place of the eye.

* The *photoelectric conductivity* of selenium was discovered in 1873 by a telegraph operator at the Valentia (Irish coast) terminal station of the transatlantic cable. The operator observed that when the selenium resistors were illuminated by the sun's rays, the galvanometer indicated changes of current in the circuits.

Active Photoelectric Effect

case of the alkali metals the normal effect so far described is superposed on it a *selective effect* (discovered by Pohl and Schott in 1910), which consists in a considerable increase in number of electrons emitted at a particular wave-length and in a particular state of polarisation of the incident wave ; this may be as much as one hundred times as great as the normal experiments on

light have shown that this phenomenon is produced by that component of the electric field of the incident light which is normal to the surface of the

photoelectric substance. Various experiments, inasmuch as photoelectric cells have been employed in practical applications according to the method which they have been applied, the effect may be

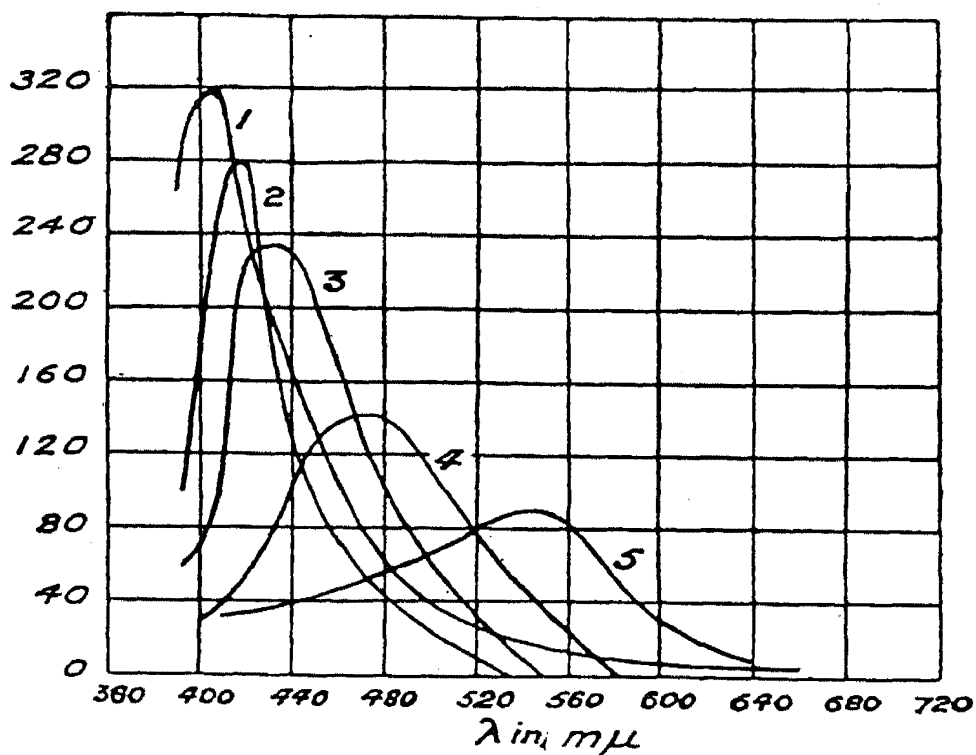


FIG. 43.

Curve 1 refers to lithium.
 „ 2 „ sodium.
 „ 3 „ potassium.
 „ 4 „ rubidium.
 „ 5 „ caesium.

rubidium, caesium, sodium or cadmium : further, the substance may be treated with a gas, such as hydrogen, in order to increase the sensitive substance is enclosed in a glass or metal tube which may be evacuated or may contain gas at a low pressure (some tenths of a millimetre of mercury) ; the gas may be lithium, neon or argon, and is introduced in order to increase the photoelectric current obtainable, taking advantage of the ionisation in the gas which gives a current far in excess of the very small current due to the photoelectrons. The advantage of proportionality between the current

and the incident luminous flux is, however, generally lost by this device.

Fig. 43 shows the relative sensitivity of the different alkali metals for various values of λ .

Photoelectric Cells and their Applications

An alkali metal photoelectric cell consists essentially of a glass bulb (or sometimes a quartz bulb) into which pass two electrodes with perfect sealing. One of these electrodes is in contact with the sensitive metal and leads to the cathode; the anode is a grid (or a ring) connected to the positive pole of either a battery of cells or accumulators, or a dynamo, the negative pole of which is connected to the cathode.

In the dark the cell is a perfect insulator, but immediately the alkali metal is illuminated, a current passes in the direction corresponding to the emission of electrons, and the intensity of the current is greater the greater the light flux received.

The metal chosen depends on the spectral region employed; it is usual to employ pure potassium (or potassium hydride) in the visible region of the spectrum, rubidium for the red rays and cadmium for the ultra-violet.

A great deal of care is taken in introducing the metal into the bulb. An interesting process is that in which the metal (sodium or potassium) is caused to pass through the glass of the bulb from the outside to the inside by electrolysis. Glass is a non-crystallised silicate of sodium in a state of very high viscosity; but this viscosity is very considerably reduced before softening occurs when the glass is heated above a certain temperature. If, now, there is an incandescent filament inside an evacuated bulb which is placed in a bath of fused sodium nitrate, electrolysis takes place and sodium ions pass into the interior of the bulb in exactly the same way as, during the electrolysis of a solution of copper sulphate, the copper travels from the anode to the cathode (which is composed of a different metal) while the solution remains unaltered.

Omitting reference to other constructional details, we may say that a cell of the ordinary kind, with an evacuated bulb,

illuminated by a lamp of 50 candles placed at a distance of one metre, will give a current of the order of one-hundredth of a microampère. The current may be ten to one hundred times as great in the case of sensitised cells ; the applied voltage may vary between 50 and 200 volts according to the type of bulb.

The current given by a cell depends on a large number of factors, e.g., the nature of the alkali metal and the nature and pressure of the gas present (hydrogen, argon or neon) when the cell is not evacuated ; it also depends on the size of the window, on the difference of potential between the electrodes, on the intensity and wave-length of the monochromatic light incident on the cell, etc. In the case of composite light the spectral distribution is naturally important.

Other conditions also affect the amount of the photoelectric current obtained, but we shall not go into further details here.

In the case of practical apparatus a study is made of the curves connecting the current with the wave-length of the incident light, assuming a constant rate of energy reception ; similarly the curves showing, for a constant light flux, the variation of current with the voltage applied to the cell are obtained ; finally, the effect of alteration of the gas pressure in a given cell is studied under conditions of constant illumination.

By avoiding all losses due to surface conductivity, and using a sensitive electrometer of small capacity, it is possible to detect extremely small amounts of luminous flux, of the order of 10^{-6} erg per second. Also the very small photoelectric currents can be amplified by means of the ordinary three-electrode valves used in wireless telegraphy, and they may then be measured by means of a galvanometer ; the cell thus forms a real *artificial eye*, the sensitivity of which exceeds that of the human eye.

The principal applications of photoelectric cells are in photometry, in the transmission of photographs to a distance, in television and in sound cinematography. These applications are based on a variation of the photoelectric current following the fluctuations which occur in a beam of light caused to move over the photograph or the scene to be transmitted or to pass through a strip at the side of the cinematograph film being shown.

As regards photometry, we may recall at once that the cell forms a kind of substitute for the human eye, but with the important difference that the maximum of the sensitivity curve of the eye is in the yellow-green ($\lambda = 0.56$

micron) while the maximum of the sensitivity curve for the cell occurs in the blue-violet.

For this reason the results are different from those given by visual observations unless the colours of the light sources to be compared are nearly the same or unless suitable coloured filters are used to reduce the difference.

In the opacimeter, cells are used to measure the opacity of an absorbing medium. This may be done by comparing the intensity of the photoelectric current produced by the luminous flux before and after passing through the medium in question, or, alternatively, by altering the intensity of the incident flux until it gives the same result as the flux which has passed through the medium.

The most important application of the photoelectric method in opacimetry is to the special branch of microphotometry, in which the photographic

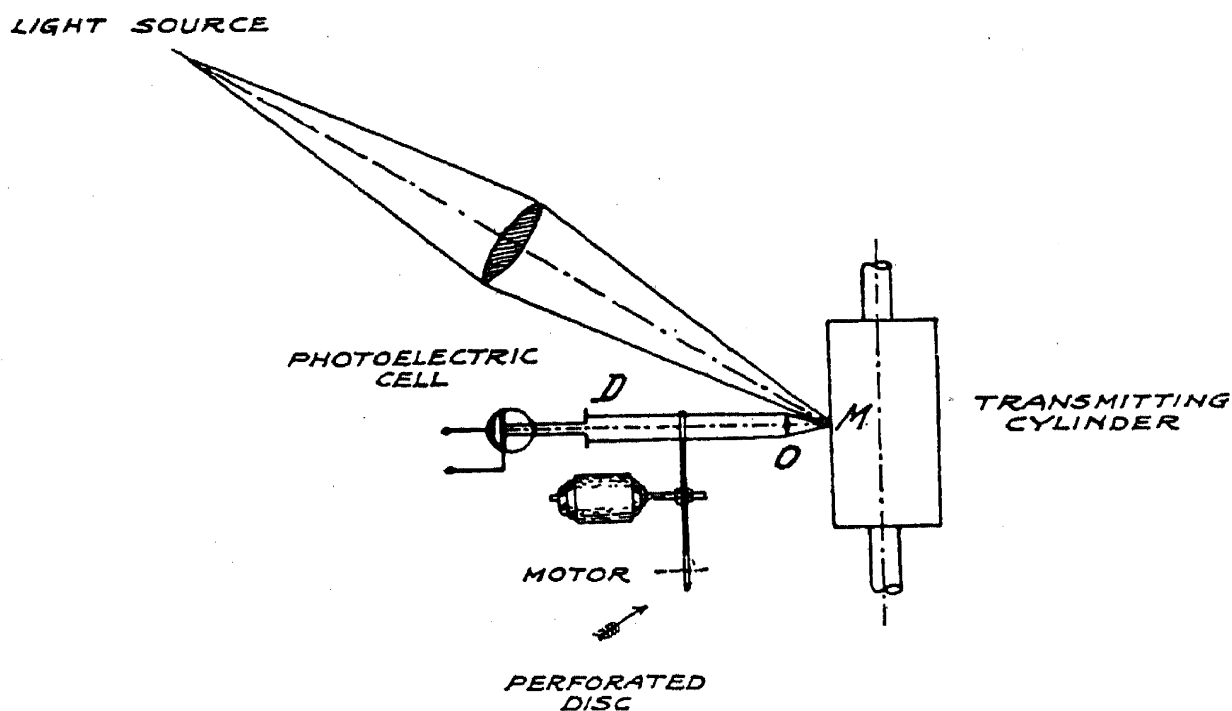


FIG. 44.—Transmitting end of Belin apparatus for phototelegraphy.

density of stellar spectra is measured and at the same time a record of the measurements is obtained automatically for the spectrum under examination; as is well known, these spectra consist of lines, and it is therefore necessary that the beam of light used to examine them in detail should be emitted from a very small aperture. This beam, after it has passed through the spectral line or band, falls on a photoelectric cell and the resulting current is measured by means of a recording galvanometer.

Phototelegraphy consists in the transmission of photographs to a distance, and should not be confused with *telephotography*, which is photography by means of a telescope objective for military or map-making purposes.

The transmission may take place over telegraph lines or by means of radio waves.

Besides photographs, such things as complete pages of journals, signatures, or documents may be transmitted; between certain cities in China it is possible to send telegrams written in the Chinese ideographic characters,

without recourse to translation into English and retranslation at the receiving station such as is necessary when using the Morse code (of dots and dashes) owing to the fact that this code is designed for the European alphabet.*

Phototelegraphy has now been adopted throughout the world, with very great advantages which we need not go into now. To-day newspapers strive to reproduce, in every country, photographs of events which take place in all parts of the globe, just in the same way as they give news received by telegraph; similarly, too, transatlantic magnates are able to present their guests in a few hours with photographs received by radio; likewise, the police in one city can telegraph to their colleagues in all parts the likeness of a criminal who is wanted.

In order to explain how the photoelectric cell provides a solution of this most difficult problem, we may take as an example the Belin system.

At the transmitting station the document to be reproduced is fastened on a cylinder which rotates at a uniform velocity and at the same time moves forward on its axis so that a fixed point traces out a helical path with an even pitch, e.g., a quarter of a millimetre (see Fig. 44).

A very small and intense spot of light is formed on the cylinder by means

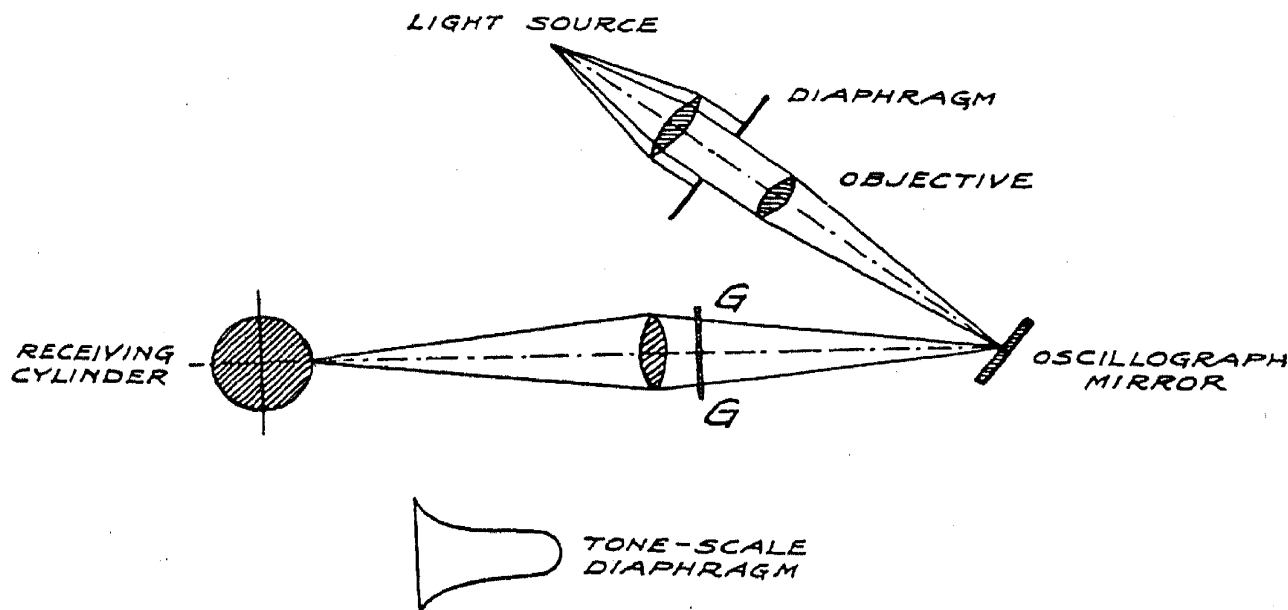


FIG. 45.—Receiving end of Belin apparatus for transmitting photographs.

of a lens and a total reflection prism; the light reflected from this illuminated spot falls on a photoelectric cell, after traversing an objective and a diaphragm which together serve to restrict the beam to that light which comes from the central portion of the illuminated spot. The intensity of the reflected light depends on the tone of that part of the document which is illuminated and the current set up in the photoelectric cell circuit varies in the same manner.

This current is amplified by means of ordinary valve amplifiers in several stages, and then, by means of a transmitter, it is conveyed on a telegraph line or is converted into radio waves. In order, however, to take advantage of the facility with which alternating or rapidly varying currents can be amplified, the photoelectric current is rendered intermittent by interrupting the beam of light which illuminates the document, using for this purpose a perforated disc rotating at a high speed. This disc is shown in the figure.

At the receiving station there is first the antenna which collects the radio waves and then an amplifying system. The sensitive surface to be acted upon

* The Chinese, in their writing, use complex symbols which represent ideas.

is fixed on a cylinder which rotates in perfect synchronism with the cylinder of the sending station and which moves forward on its axis so that there is an exact correspondence, both in velocity and in phase, between the point which has emitted the signal and the point which is to be acted upon by a quantity of light proportional to the tone at the original point (see Fig. 45).

To achieve this result, in the Belin apparatus the beam of light from a metal filament lamp, suitably concentrated, falls on an oscillograph mirror. The current received, after being amplified, passes through the oscillograph; the mirror oscillates with an amplitude which is proportional to this current and therefore also to the photoelectric current. The rectangular beam of light reflected from the mirror passes through the tone-scale diaphragm; this is a window which diminishes in breadth from a maximum to zero, and serves to augment the contrast in the final reproduction. It transmits more or less light

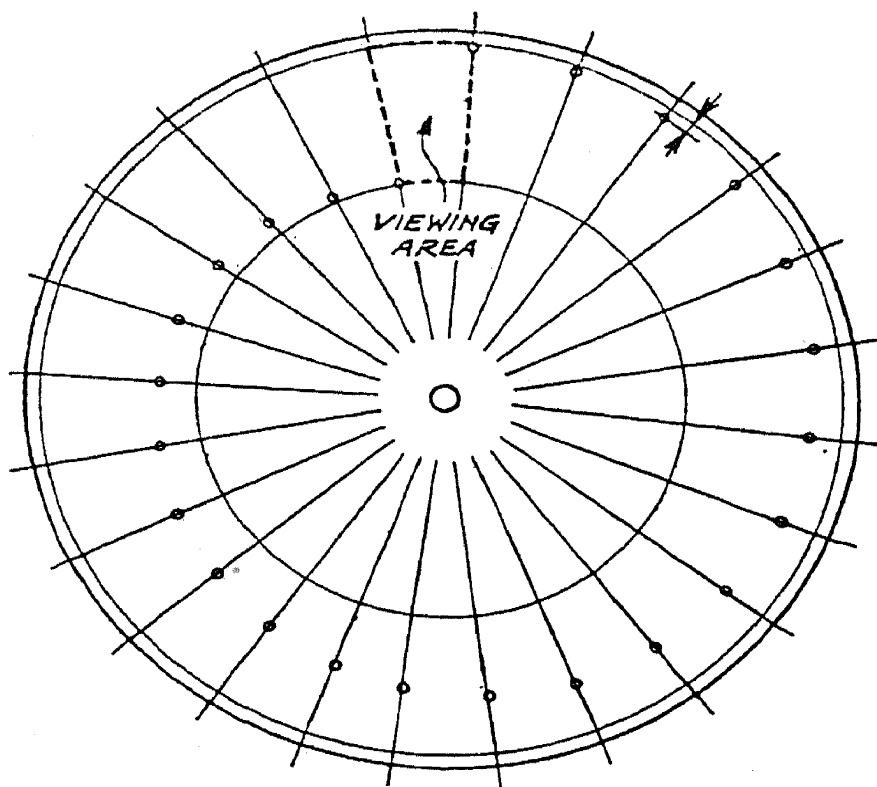


FIG. 46.—The Nipkow disc.

according as the oscillograph mirror turns through a greater or less angle and in this way the quantity of light which falls on the photographic paper is strictly governed by the photoelectric current.

We may again emphasise the important fact that the transmission of photographs to a distance, as well as television, which is simply a further development of the same process, is made possible by the fact that the photoelectric cell follows *without inertia*, i.e., without any delay, the most rapid variations in the light received by it, so that electric impulses are produced with precisely the same rhythm as the light impulses received. It is on account of their lack of this most valuable property that the older selenium cells have been abandoned.

We shall not refer to sound cinematography or to colorimetry for lack of space; for a treatment of these subjects special treatises should be consulted.

Television, as is well known, consists in the reproduction of moving figures at a distance, and it has already been combined with telephone apparatus, so

that the problem of seeing the person to whom one is telephoning has been solved ; transmission may take place either by line or by radio.

The problem of television, expressed in a few words, is as follows :—

(1) The splitting up, or, better, the “ scanning,” of the object in very small parts.

(2) The transformation into electric impulses of the light impulses corresponding to the successive portions of the object scanned and the use of these electric impulses to modulate the high frequency current from a valve transmitter.

(3) The conversion of these very rapid successive impulses of current into light impulses in such a way as to reconstruct the original object.

(4) The maintenance of absolute synchronism between transmitter and receiver.

We shall say very little about the practical systems of television ; those desiring to know more about the subject may read the book “ Television ” by the author of the present volume.

The splitting up into points of the image to be transmitted may be effected by means of the perforated disc patented by Nipkow in 1884 ; this is a rotating disc about 50 cm. in diameter and having near its edge a series of holes which are not equidistant from the centre, but are situated on a spiral (see Fig. 46).

In front of the disc is a diaphragm which is of such a size that only one hole in the disc is exposed at any given instant.

What happens when the disc rotates in front of the object to be transmitted ?

A hole moves in such a way that it scans the object in very small bands, and

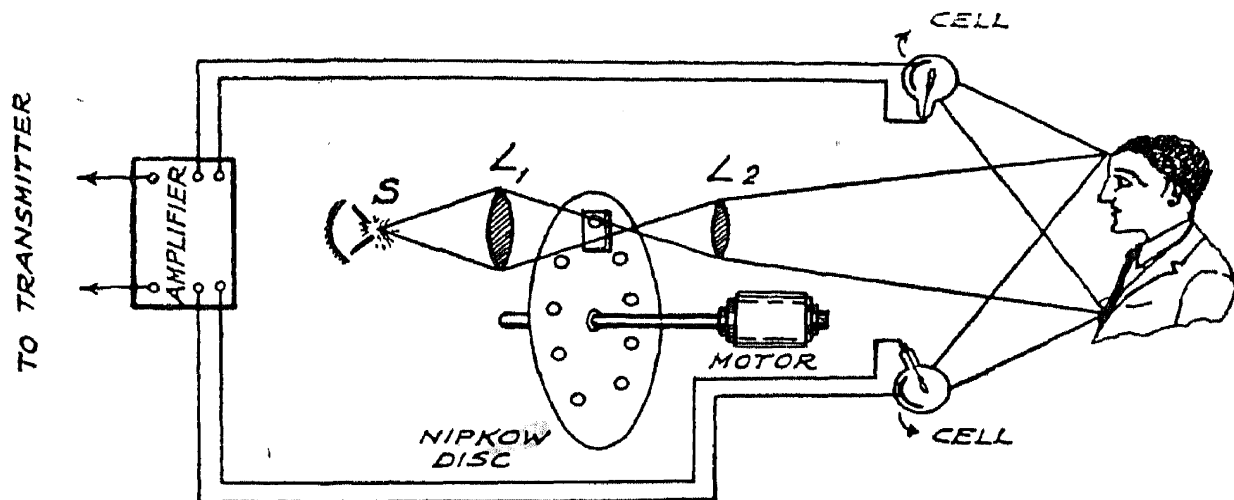


FIG. 47.—Diagram of transmitting station in television.

it transmits a narrow beam of light corresponding to the image of a very small zone of the object. If these rays, which vary in intensity according to the point of the object from which they come, fall on a photoelectric cell, this cell will convert the various light impulses into current impulses ; these currents, suitably increased by means of amplifiers, are used to modulate the high frequency current from a radio-transmitter. The waves thus generated are collected at the receiving station and there amplified and the current impulses are then converted into light by means of *neon lamps*.

The neon lamp is the pivotal element in television reception. Although neon lamps have various forms and dimensions, those used in television consist of a straight tube with two nickel plate electrodes (8 sq. cm. in area). The lamp *strikes* at about 160 volts.

As used in television, this lamp is placed in circuit with the last valve of the amplifier at the receiving station, and transforms into light impulses the variations in the plate circuit, thus responding faithfully to the fluctuations in the light which falls on the photoelectric cell of the transmitter. The

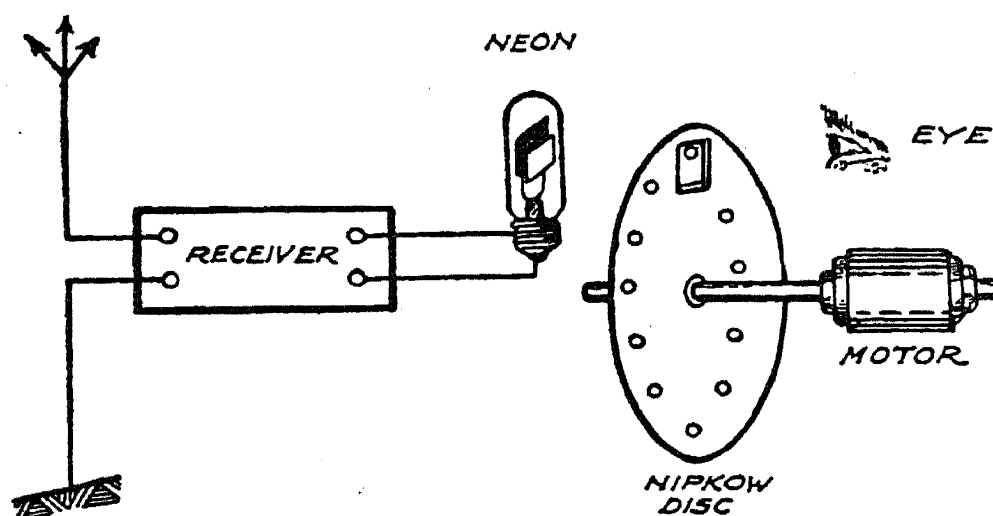


FIG. 48.—Diagram of receiving station in television.

response of the lamp is so instantaneous that brightness fluctuations may occur with frequencies up to 100,000 per second.

How is the image reconstructed at the receiving station?

The extremely rapid individual variations in the light of the neon lamp are combined to give light fluctuations which are exactly similar to those produced

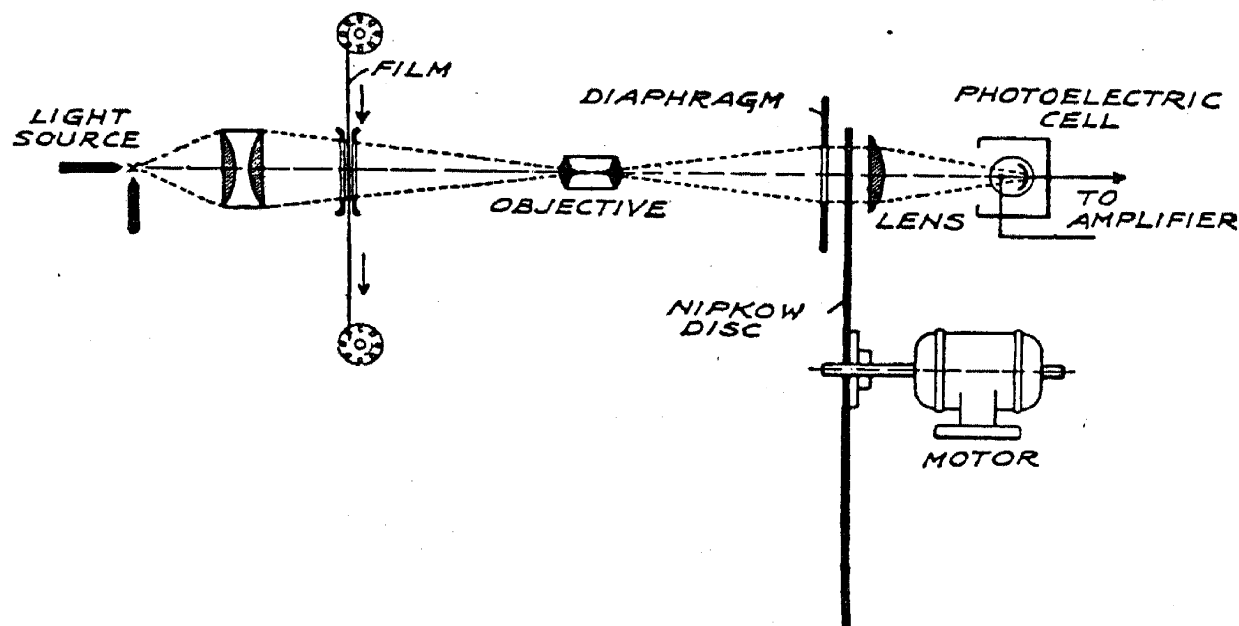


FIG. 49.—Diagram of telekinema.

by the holes in the rotating disc at the transmitting station, and the light from the neon lamp passes through a disc which is identical with the scanning disc and in exact synchronism with it. The observer stands in front of this disc and looks through a suitably arranged diaphragm (see Fig. 48). He then sees an image of the object transmitted since the individual points, separated in the process of analysis by the first disc, are recombined to form a complete picture. Although these points are seen successively, and not simultaneously,

they follow one another so rapidly that the well-known phenomenon of persistence of vision causes them to appear as a single picture. In this way, the whole object is seen.

Once the principle of television has been understood it is very easy to see how *kinematography at a distance* may be arranged; chronologically this preceded television on account of its greater simplicity. Inventors in the field of telekinematography frequently turned to television and applied to it the experience they had gained. In order to make clear how kinematography at a distance may be effected, we give in Fig. 49 a diagram of this type of apparatus; the light which passes through the moving film falls on the photoelectric cell and so produces the current used to modulate the high frequency current supplying the radio transmitter.

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CHAPTER VI

THE COMPTON EFFECT. LIGHT QUANTS

The Discovery of the Theory

DURING the year 1923 a young American physicist who is now famous, A. H. Compton, of the University of Chicago, discovered a further phenomenon which was completely in accord with the corpuscular conception of light, *i.e.*, with the theory of light quanta proposed by Einstein.

Compton observed that when a beam of X-rays fell on a body the frequency of the scattered radiation remained unaltered in the direction of the incident rays, but became lower in other directions and depended on the angle of deviation.

The theory of this phenomenon states that the scattering is brought about by the electron and not by the atom ; this theory was proposed simultaneously by Debye in Switzerland and by Compton in America.*

The primary radiations used for the experiments were the K radiations of molybdenum and tungsten ; the secondary radiators were lithium, beryllium, boron, carbon, sodium, magnesium, aluminium, sulphur, copper, silver, etc., the spectrographs of the scattered radiations, giving the analysis of their wave-lengths, were obtained either photographically or by means of the ionisation chamber.

These experiments were the first to demonstrate clearly and unmistakably the collisions that occurred between quanta of radiant energy and electrons which were, for practical purposes, free. What Compton observed was not the presence of electrons which acquired a momentum mv absorbed from the radiation (these were discovered later), but the presence of radiation of a

* A. H. Compton, *Phys. Rev.*, 22, p. 409, 1923. P. Debye, *Phys. Zeits.*, 24, p. 161, 1923.

new kind originated as a result of collisions between the original radiation and the free electron.

We have not met with anything of the kind in what has been described so far; when, in the photoelectric effect, a light quant liberates an electron from one atom, the light quant is completely destroyed and transfers the whole of its energy to the electron; the loss of its momentum is not important, since the atom takes care of this.* But when the electron is originally free, so that there is no atom to absorb the momentum of the radiation, matters are different.

What actually takes place is as follows: the energy and the momentum of the light quant are partly transferred to the electron and a new light quant of lower energy and smaller momentum (and hence of lower frequency) is formed moving in a direction inclined to that of the original light quant (see Fig. 50). It is as if a billiard ball were to

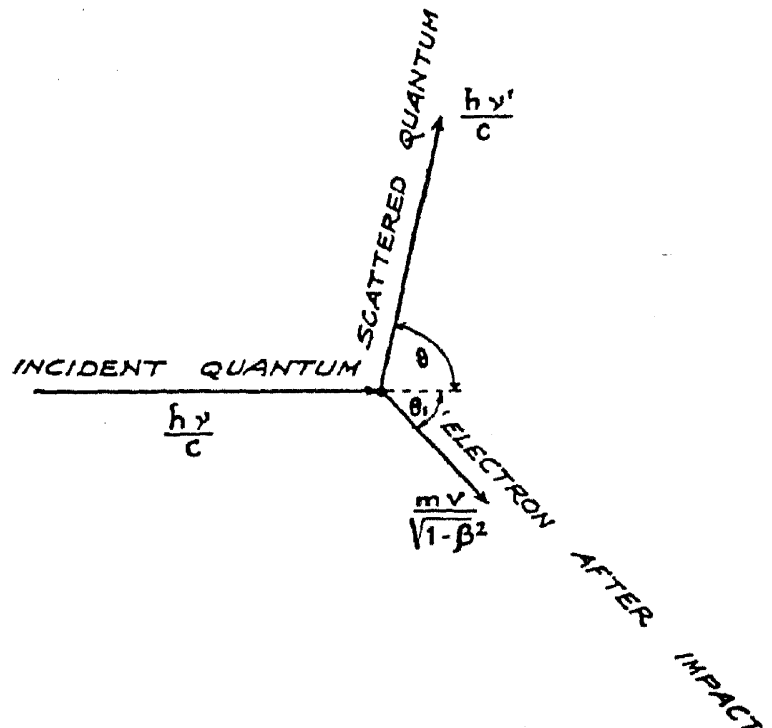


FIG. 50.

lose some of its weight on meeting another ball, in addition to changing its direction of motion.

The rules of this lilliputian game of billiards, in which the light quants are the balls which strike and the electrons those which are struck, are well defined and, in fact, the two principles

* Some years previously Einstein had already concluded, on purely theoretical considerations concerning the interaction between atoms and radiation, that the light quant should have ascribed to it a momentum $h\nu/c$ as well as the energy $h\nu$. When one atom meets another, in considering their mutual reaction it is necessary to take account of both the kinetic energy (or, more generally, the energy) and the momentum: the colliding atom, in fact, is defined by its mass and its velocity, or by its energy and its momentum.

Now let us consider an atom which, on being struck by a light quant, absorbs the whole of the energy $h\nu$: this atom must also absorb the momentum, the value of which is not independent of the energy, but is necessarily equal to $h\nu/c$.

of the conservation of energy and the conservation of momentum must be obeyed.

The first principle demands that the energy $h\nu$ of the incident light quant shall be equal to the sum of the energy of the scattered (or deviated) light quant, $h\nu'$, and the kinetic energy W of the electron which flies off.

The value given for W by the theory of relativity is

$$W = m_0 c^2 \left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right),$$

where m_0 is the mass of the electron and $v = c\beta$ its velocity.

The equation expressing the conservation of energy may therefore be written :

$$h\nu = h\nu' + m_0 c^2 \left(\frac{1}{\sqrt{1 - \beta^2}} - 1 \right) \quad . \quad . \quad . \quad (1)$$

The principle of the conservation of momentum demands that the momentum of the incident light quant shall be equal to the resultant of the momentum of the deviated light quant and that acquired by the electron. Since momentum is a vector, this condition gives two equations, and not one, connecting the various quantities involved, as we shall see presently.

It will be useful here to remark that, since the energy of a light quant is $h\nu$ and since it travels with the velocity of light, c , its momentum is $h\nu/c$, since by Einstein's law : $E/c^2 = \text{mass}$ (and therefore $E/c = mc$).

In comparison with this energy $h\nu$, which is large for high frequencies, the energy which binds the electron to its atom is negligible and so the impact may be considered to occur as if the electron were free.

The momentum of the electron is $m_0 v / \sqrt{1 - \beta^2}$, and the conservation of the original momentum, $h\nu/c$, leads to the following two equations :

$$\frac{h\nu}{c} = \frac{h\nu'}{c} \cos \theta + \frac{m_0 v}{\sqrt{1 - \beta^2}} \cos \theta' \quad . \quad . \quad . \quad (2)$$

$$0 = \frac{h\nu'}{c} \sin \theta + \frac{m_0 v}{\sqrt{1 - \beta^2}} \sin \theta' \quad . \quad . \quad . \quad (3)$$

The former refers to the direction of the incident radiation, while the latter refers to the direction at right angles to this.

If the two quantities θ' and ν be eliminated between the three equations written above, the result is the required relation between the two frequencies ν and ν' , *i.e.*, between the frequency of the primary X-rays on the one hand, and that of the X-rays *scattered at a given angle* on the other hand. The result is as follows :

$$\frac{\nu'}{\nu} = \frac{1}{1 + (h\nu/m_0c^2)(1 - \cos \theta)} \quad \dots \quad (4)$$

If the wave-length relation is required instead of the frequency, by putting $\lambda = c/\nu$ the following important relation is obtained :

$$\lambda' - \lambda = (h/m_0c)(1 - \cos \theta) = 0.024 (1 - \cos \theta) \quad \dots \quad (5)$$

where λ is expressed in Ångströms. This is the fundamental equation of the Compton effect.

The kinetic energy of the electron after the impact can easily be found to be

$$E_{\text{kin.}} = h\nu \frac{1 - \cos \theta}{1 + \alpha (1 - \cos \theta)} = h\nu \frac{2\alpha \cos^2 \theta'}{(1 + \alpha)^2 - \alpha^2 \cos^2 \theta'} \quad (6)$$

where $\alpha = h/m_0c\lambda$.

As will be seen, the change $\Delta\lambda = (\lambda - \lambda')$ which takes place in the wave-length of the scattered light quant cannot be determined *a priori* since the angle through which the radiation is scattered appears in the formula (5); this, however, does not lessen the value of the result in any way. All that can be said is that if the light quant travels in the direction θ , the change of wave-length is that just written.

The value $\Delta\lambda$ can be found for any angle θ and can then be compared with the value found experimentally; the agreement has been found to be perfect and we shall not stay to describe the tests carried out; the method consists in causing the beam of scattered rays to fall on an X-ray spectroscope; the beam is thus deflected towards an ionisation chamber acting as a detector, or else on to a photographic plate, and the point of the plate affected (or, alternatively, the position of the ionisation chamber) enables the wave-length to be found at once. In order to demonstrate the

verification of the theory, a mark may be made on the photographic plate at the point at which theory indicates that the beam should strike it if the Compton effect does not exist, *i.e.*, if there is no change of frequency ; this, however, is unnecessary, since actually there is always a line produced by the radiation which is not changed in frequency—the primary radiation—and the comparison desired thus follows automatically.

The experimental apparatus used for studying the Compton

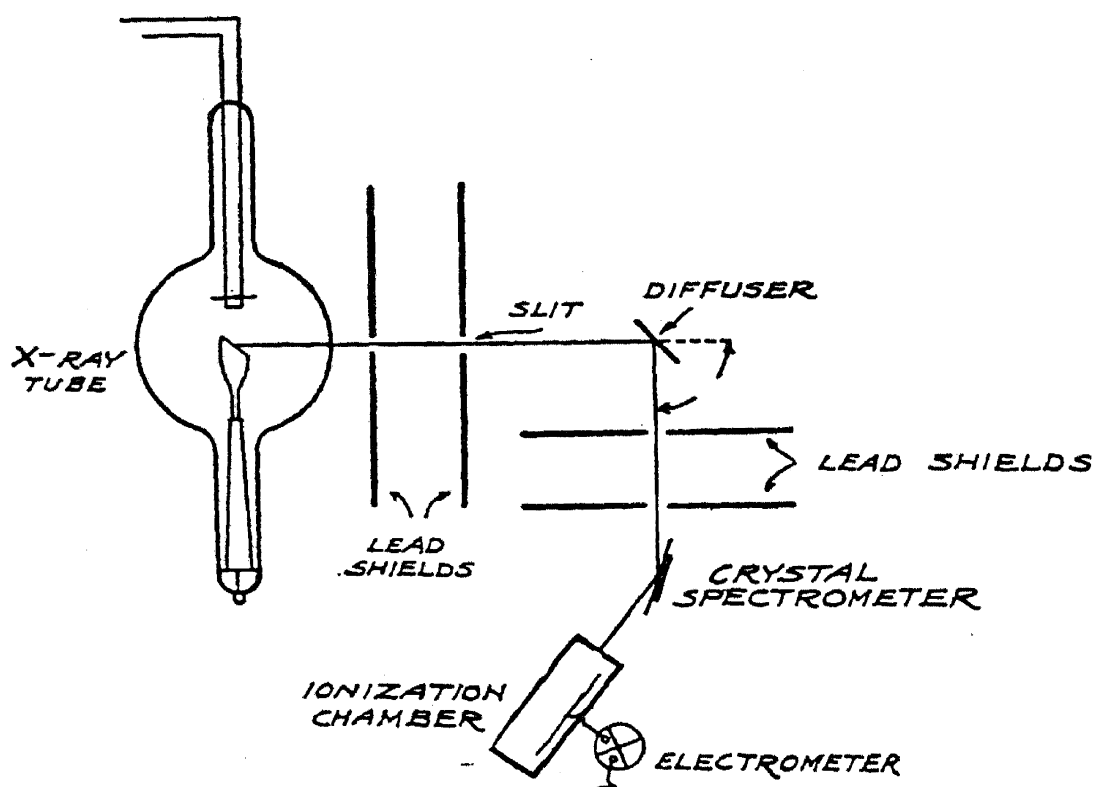


FIG. 51.

effect consists, then, of two parts ; the first part comprises an X-ray tube, screens with small apertures, and a crystal which picks out and provides the monochromatic wave-length which is to be studied and which falls on the scattering substance : the second part of the apparatus consists of a rotating crystal spectrograph by means of which the X-rays scattered by the block of material may be examined.

Now let us return to the important relationship

$$\lambda' - \lambda = 0.024 (1 - \cos \theta) \quad \text{in \AA ngstr\"om units.}$$

This states that the change in the wave-length is independent of the scattering material and also of the wave-length of the incident

radiation ; it is therefore the same for all the X-rays used. The maximum value of $\lambda' - \lambda$ occurs when $\theta = 180^\circ$, *i.e.*, when the light quant turns back on to its own path and in this case

$$\Delta\lambda_{\max} = 0.048 \text{ \AA}.$$

This change is a small fraction of the incident wave-length for large values of λ , but it may, on the other hand, be equal to several times λ if this quantity is very small, as in the case of hard X-rays and γ -rays.

To sum up, when an atom is struck by Röntgen radiation of frequency ν it may become a source of secondary radiation of two kinds :

- | | | | |
|----------------------------|---|--------------|----------|
| (a) Wave radiations | $h\nu$ | $h\nu_A$ | $h\nu'$ |
| | unaltered | fluorescence | Compton. |
| (b) Corpuscular radiations | $\left\{ \begin{array}{l} \text{photo-electrons} \\ \text{recoil electrons accompanying the} \\ \quad h\nu' \text{ radiation.} \end{array} \right.$ | | |

Verifications of the Compton Effect

Compton verified equation (5) experimentally,* using as incident radiation the characteristic X-rays from an anticathode of molybdenum and as scattering material the free—or practically free—electrons of graphite, lithium or aluminium ; he found actually that the K_α ray from molybdenum was displaced towards the longer wave-lengths, as predicted, and by the amount calculated.

According to the theory, the displacement should be independent of the nature of the scattering material since the effect is due to the mutual action between radiation and loosely bound electrons ; this independence was actually found, as shown by the table on p. 202.

The theoretical change $\lambda' - \lambda$ can be calculated, as we know, by means of formula (5) :

$$\lambda' - \lambda = \frac{h}{m_0 c} (1 - \cos \theta) = \frac{2h}{m_0 c} \sin^2 \frac{\theta}{2}.$$

* See also H. Kallman and H. Mark, *Naturwissenschaften*, 13, p. 297, 1925. H. Sharp, *Phys. Rev.*, 26, p. 691, 1925.

Diffuser.	Primary Radiation in cm. $\times 10^{-11}$.	Angle θ .	$\Delta\lambda$ observed in cm. $\times 10^{-11}$.	$\Delta\lambda$ calculated in cm. $\times 10^{-11}$.
Graphite .	} K_α molybdenum = 708	30°	3 ± 1	3.2
Graphite .		60°	12.0 ± 1	12.2
Aluminium .		90°	24.4 ± 1	24.3
Aluminium .	} K_β molybdenum = 630	90°	24.2 ± 1	24.3
Sulphur .		90°	24.0 ± 5	24.3
Silver .	} K_α molybdenum = 708	90°	23.8 ± 2	24.3

We will now continue our consideration of the theory.

Once the value of v (velocity of recoil of the electron) has been found from the two fundamental equations (1) and (2) established above, it is easy to express the angle θ' which the path of the electron struck by the incident light quant makes with the direction of incidence of that light quant.

By a very easy calculation from equations (1), (2) and (3), it may be shown that

$$\tan \theta' = - \frac{1}{1 + \alpha} \cdot \frac{1}{\tan \frac{1}{2} \theta} \quad \dots \quad (7)$$

where $\alpha = h/mc\lambda = 0.0242/\lambda$.

It follows that, while the light quants are scattered at all angles

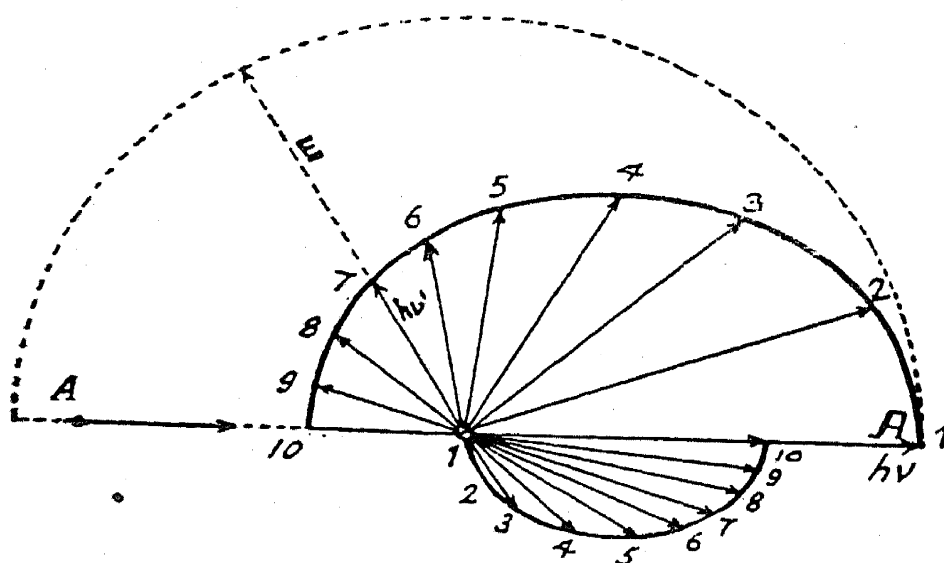


FIG. 52.

between 0° and 180° , the corresponding electrons start off in directions all of which lie between 270° and 360° , i.e., all the

electrons recoil in the forward direction if their motion is accompanied by scattered radiation.

In the case for which $\theta = 0$ there is no change in the energy of the scattered light quant. For $\theta = 180^\circ$, when the incident light quant reverses its direction of motion, it suffers the maximum loss of energy, the electron recoils in the forward direction so that the angle $\theta' = 0$ and with a maximum of energy.

The results obtained may be summarised in a diagram (Fig. 52.)

The diagram illustrates the relations between (i) the energy ($h\nu$) of the primary light quant (incident along AA), this energy being indicated by the radius of the dotted circle, and (ii) the energy $h\nu'$

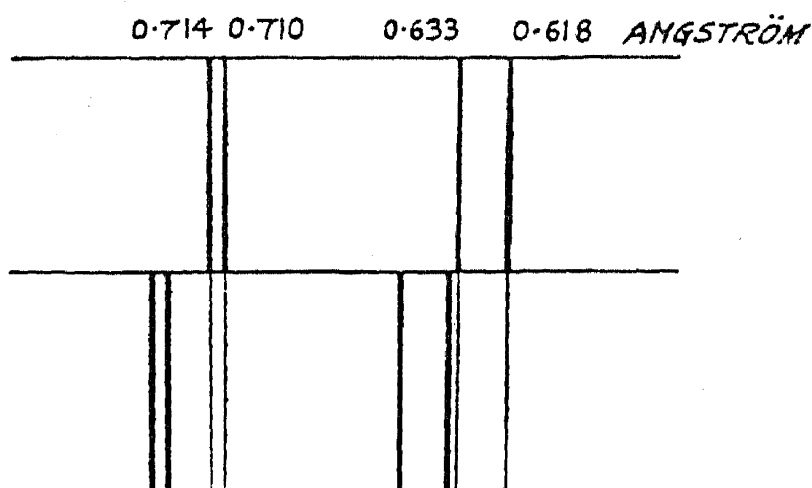


FIG. 53.

of a light quant scattered in various directions as shown by the points on the upper full-line curve. It has been seen that all the electrons recoil in the forward direction. For any direction of scattering, the lower curve gives the energy of the recoiling electron; it is only necessary to refer to corresponding radii vectores which are similarly numbered.

In the diagram of Fig. 53 the upper portion shows the K spectrum of molybdenum composed of four lines, 0.714, 0.710, 0.633, 0.618 Ångström; below it is shown the secondary spectrum obtained at 90° by scattering from aluminium, so that, corresponding to every upper line, there are two lower lines, one of which has the same wave-length as the line above, while the other is displaced by an amount $\lambda' - \lambda = h/m_0c = 0.024$ Ångström.

Fig. 54 shows, on the other hand, the rays scattered at 90° when the K_α line of molybdenum falls on the four elements carbon, aluminium, copper and silver.

The relative intensities of the two lines, the "unmodified" and

C AT 90° AL AT 90° Cu AT 90° Ag AT 90°

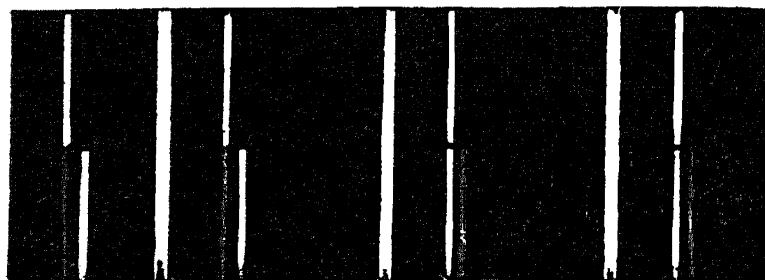


FIG. 54.

the "modified," are known to represent the ratio between the numbers of light quants which are deflected by collision with a free electron and of those which are reflected as from an

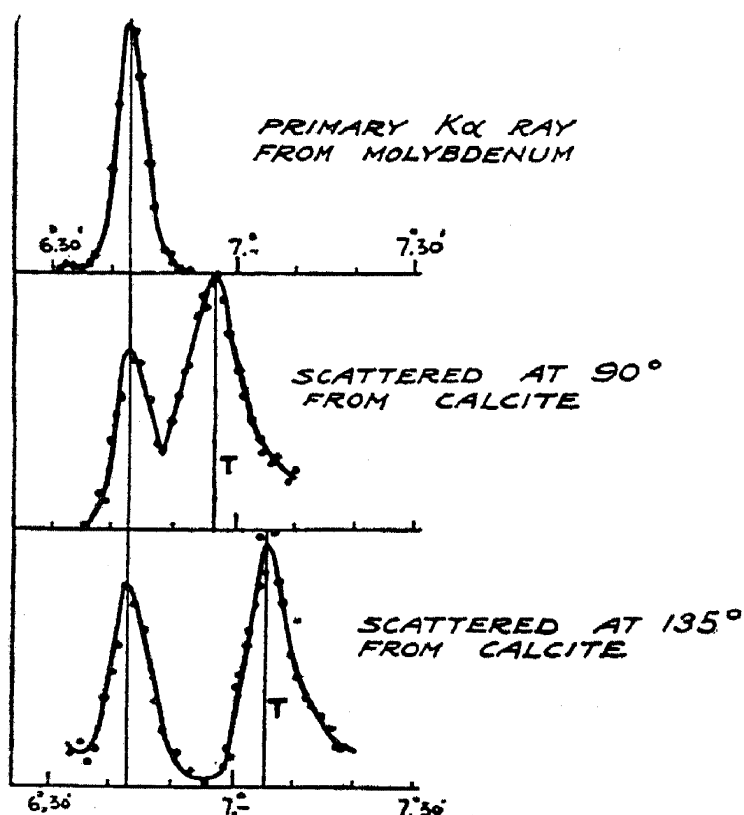


FIG. 55.

immovable object; the diagrams show that this ratio varies considerably in passing from the light elements (carbon) to the heavier ones (silver); thus, while the greater part of the light quants scattered by lithium show the calculated change of wave-

length, nearly all those scattered by lead emerge with the same frequency as the incident radiation; the Compton effect, then, loses more and more of its importance the further we proceed in the periodic classification.

It is also to be noted that, for any given body, the relative intensity of the two radiations depends on the directions of scattering under consideration; this is illustrated in Fig. 55, in which the ordinates represent quantities which are proportional to the intensities of the radiations, these intensities being given by the amounts of ionisation produced in the ionisation chamber.

These curves, obtained by using the K_α radiation from molybdenum, indicate, first, the perfect agreement between the experimental results and the theoretical value deduced from the separation of the two wave-lengths; this value is shown on the axis of abscissæ. Secondly, the diagrams for 90° and 135° show the relative proportion between the intensity of the most modified radiation and that of the partially modified radiation.

The ordinate T shows the calculated position of the modified wave-lengths.*

* The scattered radiation which shows the reduced frequency effect is thus always accompanied by radiation of the same frequency as that of the primary beam, *i.e.*, that to be expected on the classical theory. At first sight it seems difficult to reconcile this with the simple theory of the Compton effect; but an explanation, at least of a qualitative nature, can be given. In deducing the fundamental formula giving $\lambda' - \lambda$ the action considered was that between the incident light quant and the *free* electron, and the energy required to liberate this electron from the forces binding it to the atom were very small compared with the energy $h\nu$. When X-radiation for which $h\nu$ has a very high value is employed in the primary beam, there must be a large number of electrons for which this supposition is justified and the Compton effect is then produced.

There are, however, other electrons which are tightly bound in the inner parts of the atom and when the radiation acts on these, its energy quantum $h\nu$ is insufficient to liberate them so that the electron forms part of the atom; the mass m_0 which occurs in the calculation of $\Delta\lambda$ is thus no longer the mass of the electron, but the much larger mass of the atom; $\Delta\lambda$ becomes imperceptibly small. This accounts, therefore, for the radiation which shows no change of frequency.

It will also be understood that this result will be more noticeable the heavier the atoms which are struck by the radiation, for in these atoms the electrons are bound very firmly; it will also be more pronounced for *soft* primary radiation than for *hard* rays.

This, again, explains why the Compton effect is not observed in the visible spectrum; actually if $h\nu$ is so small that even the most loosely bound electrons in atoms of low atomic number (*e.g.*, those in paraffin) can be regarded as free, $\Delta\lambda$ becomes of the order of 10^{-5} Ångström, and is therefore undetectable.

Compton has also studied the scattering due to the electrons bound to the atom and has found that in this case the formula :

$$\Delta\lambda = \frac{2h}{mc} \sin^2 \frac{\theta}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

becomes
$$\Delta\lambda = \frac{\lambda^2}{\lambda_i - \lambda} + 2 \frac{h}{m_0 c} \sin^2 \frac{\theta}{2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where λ_i is the wave-length corresponding to the ionisation potential V of the electrons considered, *i.e.*, that defined by

$$h\nu_i = h(c/\lambda_i) = V \cdot e.$$

In note * we shall show how formula (2) may be deduced ; this formula represents the experimental results exactly, without any limitations, while formula (1) shows good agreement with experiment only in the case of scattering substances having a low atomic weight.

Another part of the theory which could only be verified by very delicate experimental procedure was the existence of the recoil electrons and their distribution.

In a gaseous scattering material, *e.g.*, air, besides the electron shot forward in accordance with the theory there are also electrons which have a photoelectric origin ; now the range of an electron in a gas is proportional to the square of its kinetic energy and is approximately equal to the energy of the incident light quant ($h\nu = \frac{1}{2}mv^2$) if the energy which binds the electron is negligible in comparison with the value of $h\nu$. It may be concluded that the path of the photoelectric electrons is constant. The recoil electrons, however, have velocities which are smaller than those of the photoelectrons since they only take up a portion of the energy of the incident light quant and travel through the gas for distances which become smaller as the angle of deviation from the direction of incidence increases.

This provides a criterion which is sufficient to distinguish one

* Since the energy E of a light quant with frequency ν is $h\nu = hc/\lambda = E$, it follows that $-(hc/\lambda^2)d\lambda = dE$, *i.e.*, $\lambda^2 dE = -hc d\lambda$. Since the difference of energy may be represented by $hc/(\lambda_i - \lambda)$, it follows that $\Delta\lambda = \lambda^2/(\lambda_i - \lambda)$.

class of electrons from the other.* Wilson† and Bothe had already stated that in the clouds obtained in Wilson's method of studying ionisation in gases, there were very short tracks which could be explained as due to recoil electrons; Compton repeated these results and verified the correctness of his theory. If the track of a recoil electron and that of the photo-electron produced by the scattered light quant be recorded on the same stereoscopic

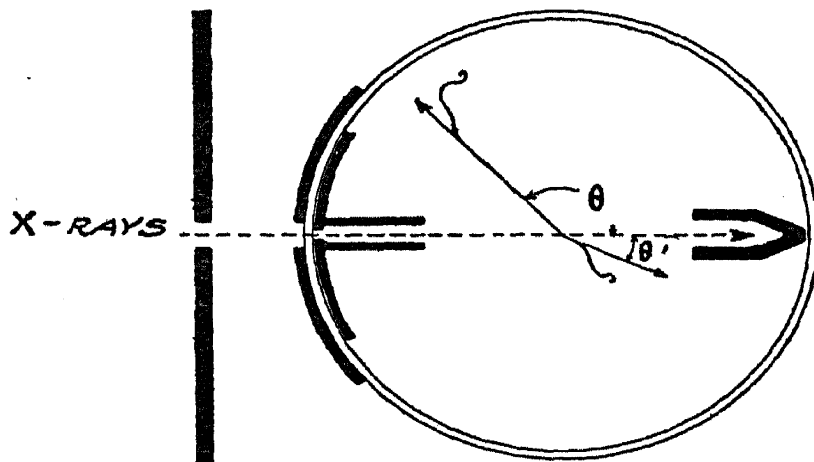


FIG. 56.

photograph, it may be verified that the angles θ and θ' obey the theoretical law found originally :

$$\tan \theta' = - \frac{1}{1 + \alpha} \cdot \frac{1}{\tan \theta/2} \quad \text{where } \alpha = \frac{0.0242}{\lambda}$$

As shown in Fig. 56, the straight line drawn from the origin of the track of the recoil electron to the origin of the track of the photo-electron liberated by the scattered light quant gives the angle θ ; the tangent to the track of the electron at its origin gives the angle θ' . Painstaking experiments carried out by Compton and Simon showed that these two angles obeyed formula (4) which had been deduced from the theory, a fact which was of the very greatest importance.

If the scattered rays, instead of obeying Compton's corpuscular

* For instance, if we take the case of *hard* X-rays for which $\lambda = 0.243$ Å., then $\nu'/\nu = 10/11$, and if the radiation is scattered at right angles to the primary beam, the energy transferred to the electron is $h(\nu - \nu') = h\nu/11$. See the accurate work of A. Bless on the energy of the expelled electron in *Phys. Rev.*, 30, p. 871, 1927.

† C. T. R. Wilson, *Roy. Soc. Proc.*, 104, pp. 1 and 192, 1923. W. Bothe, *Zeits. f. Phys.*, 16, p. 319, 1923; 20, p. 237, 1923.

rule, consisted of spherical waves, they would necessarily produce an effect in all directions and there would be no connection between the direction in which a photo-electron appeared and that in which the original electron recoiled. The importance of this experiment as a confirmation of the corpuscular nature of Einstein's light quanta will thus be appreciated.

Among the many experiments on the Compton effect, having for their object the verification of the theory of Debye and Compton which we have described, those of Bothe and Geiger (1925) are of the greatest importance; the result of these was to show that the emission of the photo-electron due to the scattered radiation—when this fell on some material—took place simultaneously with the ejection of the electron due to the primary radiation. A theory due to Bohr, Kramers and Slater,* which we shall not describe here, had led to the contrary conclusion that this rigid time relationship between the two facts should not exist, *i.e.*, the two processes should take place independently of each other; a crucial test deciding between the theories would be available if the instant at which the two electrons were emitted could be determined experimentally. This was done by Bothe and Geiger with the apparatus which we shall briefly describe.† The ionisation produced by the passage of a single electron may be detected by a counter of the type originally used by Rutherford and Geiger to count the α -particles (see p. 291 of Vol. I).

Bothe and Geiger caused a narrow beam of X-rays to pass through hydrogen and used two counters placed face to face, one being used to detect the recoil electron e and the other to detect the scattered radiation $h\nu'$. The second counter was closed with a piece of platinum foil 0.02 mm. thick and so was shielded from the recoil electrons, whilst the photo-electrons expelled by the radiation $h\nu'$ were emitted from the internal surface of the foil. The first counter, on the other hand, was open and the narrow incident beam passed between the two.

It is not to be expected that in this experiment there will be

* N. Bohr, H. A. Kramers and J. C. Slater, "The Quantum Theory of Radiation," *Phil. Mag.*, 47, p. 785, 1924, and *Zeits. f. Phys.*, 24, p. 69, 1914.

† See *Zeits. f. Phys.*, 26, p. 44, 1924, and 32, p. 639, 1925.

equality between the impulses on the electrometer connected to the counter taking the $h\nu'$ and those on the electrometer connected to the counter affected by the recoil electrons, because only a fraction of the scattered radiation liberates photo-electrons ; the vital point of the experiment is to determine whether the $h\nu'$ impulses coincide with impulses of the electron counter ; actually Bothe and Geiger found that each signal due to $h\nu'$ coincided with the eleventh impulse on the electrometer recording the recoil electrons.

Further Consideration of Light Quants (Photons). The Crisis in the Wave Theory of Light

In view of the results obtained in the study of the Compton effect, is it now necessary to admit that radiant energy travels through space in units which are granular and separate and each of which possesses, for radiation of a given frequency ν , always the same energy $h\nu$ and always the same momentum $h\nu/c$?

The phenomena which we have described would certainly seem to force the physicist to this conception.

Einstein, taking into account the photoelectric effect and adopting as his starting point Planck's early hypothesis that radiant energy was emitted and absorbed in whole quanta, each containing a number of ergs equal to $h\nu$, boldly stated (1905) that radiant energy flux consisted of discrete quanta, not connected with each other, and travelling with the velocity of light ; these are called "light quants," although it must not be understood by this term that they exist only for visible light ; they preserve their identity, as they travel through space, from the instant of their emission to that of their absorption.

This is clearly a return to the Newtonian theory of emission, but with the difference that the particles of light may contain quantities of energy which can vary without limit, depending on the quantity ν which characterises each kind of particle.

On the other hand, we know that a very large number of different optical phenomena are easily and completely explained on the hypothesis that light, or rather all radiant energy, is a vibratory movement which spreads out in space and in which the

quantity ν , and the other quantity λ connected with it, have a simple and concrete significance, the former representing the number of vibrations per second, while the latter represents the wave-length. The wave theory, in fact, explains the reflection, refraction, interference, diffraction, polarisation, etc., of visible and invisible rays, and it is difficult to understand how the quantum theory can give an equally simple and easy explanation of any one of the phenomena just mentioned, with the possible exception of reflection. Thus, taking the case of the typical phenomenon of interference, it is more than difficult to see how this can occur except as the result of a combination of oscillations; if light consists of waves it is understandable that the superposition of one light on another which is opposed to it in phase may result in darkness; if, however, it consists of projectiles, how can these cancel one another in the dark fringes due to interference or diffraction? Further, a light quant which travels through space carrying energy equal to $h\nu$ is characterised by the quantity ν which is borrowed from the wave theory where it has a definite meaning; but what is the meaning of ν in Einstein's theory? The number ν becomes simply a numerical coefficient which is different for each of the different kinds of light quants in existence. While this is true, it is equally true that a series of phenomena give evidence in favour of light quants and would be unexplainable on the basis of the wave theory, just as interference is unexplainable on the quantum theory; the Compton effect is an outstanding case.

This position was already being discussed in 1910, and the period from then until 1927 was a critical one for Physics; to-day this crisis seems to have been surmounted, not in consequence of fresh discoveries but, strange to say, as the result of the emergence of a different way of looking at things. However, we must now resume our discussion.

It is known that two rays cannot interfere unless they emanate from one and the same centre of emission; the difference in path between the two may then amount to one or two million wave-lengths without the rays losing the power to interfere with each other, although this path difference corresponds to a

displacement of the order of a metre ; over distances such as these the phase remains unaffected ; it is difficult to understand how light quants, which leave a centre of emission successively and independently of one another, can possess this property of mutual action.

This fact leads to the idea that the dimensions—in length—of the photons may be large, *e.g.*, of the order of one metre.*

As regards similar considerations concerning the transverse dimensions of light quants, we may say that if one of two halves of a telescope objective be covered, the image of a star becomes slightly larger than when both halves of the objective are uncovered, owing to the fact that under the latter conditions certain portions of the star image disappear, owing to the interference of rays passing through the two halves of the objective. It is to be supposed, *a priori*, that interference is impossible with a quantum structure of radiant energy unless the portions which interfere all belong to a single *light quant*: considering the dimensions of telescope objectives, it thus follows that the transverse dimensions of light quants must be several centimetres. In that case, however, it is impossible to understand the action of these gargantuan light quants on our eyes when we observe a star directly, for they must necessarily pass through the pupil of the eye, and this is small compared with the dimensions we are considering.

Again, if we think of these particles of energy as being absorbed by an atom in the photoelectric effect, or if we consider the Compton effect in which a light quant strikes an electron with a single isolated blow, we are led to ascribe exceedingly small transverse dimensions to the light quant ; the difficulty is that the phenomena of interference and of diffraction, on which the wonderful wave-theory of light is founded, demand that the wave-trains shall be of considerable width ; in fact, these phenomena could not occur if the radiations were corpuscular or filamentary.

To take another example of diffraction, consider an opaque screen with a slit through which light is passing, and suppose that the breadth of this slit is 0.5 mm. If light consists of

* The name *photon* was given to light quants by G. N. Lewis in 1926.

photons which have the dimensions of an atom or of a wavelength, these photons will follow one another through the slit like droplets or grains of sand passing through an opening, and if they are moving in parallel paths before reaching the slit they will continue to move parallel to one another: the beam will maintain a constant cross-section. We know, however, that actually the beam becomes larger and gives rise to a special distribution of intensity, which is the same as that which would be expected if the wave-front were much wider than the window; moreover it becomes larger independently of the particular form of the window.

On these considerations, it would appear that the light quant must be wider than the widest slit which can exhibit the phenomena of diffraction, and this implies a width of at least 1 mm.

This, however, is not all with regard to the limiting width. Cut a second window, parallel to the first, in the same screen and at a distance d from it; where the rays, broadened out by diffraction, become superposed, interference fringes are produced exactly as if the breadth of the wave-front were greater than the distance d .

The light quant, then, would seem to be larger than the maximum distance between two slits which can give rise to interference; in fact the slits may be very widely separated and the rays passing through them superposed by means of prisms and lenses; Michelson's method for measuring the diameters of stars is of this kind: he obtains interference fringes when the two rays of light are taken from portions of the wave-front 6 metres apart.

On this basis the light quant should have a diameter of 6 metres; and can it be this which gives up the whole of its energy to an atom which is one ten-millionth of a millimetre in diameter? Is it this which takes part in a collision with an electron which is 10,000 times smaller still?

Such was the state of affairs until 1927.

There were two theories in the field, each successful in certain directions.

Whilst the wave-theory was perfectly adapted to explain interference, diffraction, polarisation and all the inexhaustible

range of phenomena presented by the classical system of optics, it seemed to be insufficient to account for what took place whenever the action of light on a single atom was under consideration ; it took no account of emission or absorption.

When the origin of a sound is investigated, it is found that it comes from an oscillator vibrating with the frequency of the sound itself, but if the origin of a luminous ray or an X-ray be examined, it is found that the frequency is associated with the stationary states of the atom ; this result is alien to the wave-theory, and hence this theory is incapable of explaining the *origin* of electromagnetic waves.

The case of absorption is similar : on the wave-theory absorption is necessarily a continuous process, if the conservation of energy be assumed, for at any point in the wave-front there is not sufficient energy to cause the atom to pass from one energy level to the next higher level. On the other hand, all the tests available are in conflict with the idea that an atom may have, for any considerable length of time, a quantity of energy intermediate between that appropriate to two stationary states, and if such intermediate conditions cannot persist a process of gradual absorption is impossible.

Contemporary physics was really faced with an extraordinary state of affairs in which two valuable theories existed simultaneously, not so much in conflict as in complete disharmony ; the two conceptions—the wave theory and the quantum theory—could not be antagonistic because there was no ground common to both. To-day, as we have said already, the situation is vastly improved, and we shall see the reason for this on p. 222.

Experimental Researches to Establish the Corpuscular Nature of Light. The Experiment of Joffé and Dobronrawoff (Leningrad, 1925) *

In order to fix our ideas let us consider a point source S emitting n light quants per second.

The number of these light quants which, in each second, hit a

* A. Joffé and N. Dobronrawoff, *Zeits. für Physik.*, 34, p. 889, 1925.

target subtending a solid angle Ω at S is, on the average, equal to

$$N = \frac{n\Omega}{4\pi},$$

since the complete solid angle about a point is 4π ; this assumes a random distribution of the light quants in all directions.

In order to make the time interval between the two blows an observable quantity, this interval T, which is given by $4\pi/n\Omega$ since it is the reciprocal of N, must be made sufficiently large by making $n\Omega$ sufficiently small.

With ordinary light the experiment would be extremely difficult on account of the small value of the quantum. Joffé and Dobronrawoff therefore had recourse to X-rays. In a tiny Röntgen tube, 8 mm. in diameter, the stream of electrons was generated by photo-electrons accelerated in a field of 12,000 volts applied between the cathode and the aluminium anticathode. The cathode was illuminated by ultra-violet light producing photoelectrons at the rate of about one thousand per second.

The receiver, or detector of the X-rays, consisted of a particle of bismuth having a radius of between 10^{-4} mm. and 4×10^{-4} mm. suspended in a Millikan condenser, in other words, it was in equilibrium in an electric field between two parallel plates. This particle of bismuth was first of all charged positively to its maximum extent so that it could not lose any more electrons, either by friction or by illumination with ultra-violet light, and thus only Röntgen radiation of sufficiently high frequency could, by causing a further ionisation of the surrounding medium, disturb the equilibrium of the particle. It therefore formed a highly sensitive detector of X-rays.

The experimenters found that, on the average, it was 30 minutes from the time at which the cathode bombardment was begun before the bismuth particle lost an electron due to the action of the incident Röntgen rays; in the absence of these rays the particle retained its charge for hour after hour.

Let us now return to the expression $T = 4\pi/n\Omega$, in which n is 1,000; the particle was at a distance of 0.2 mm. from the

anticathode so that the solid angle subtended by a particle having a mean radius of 2.5×10^{-4} mm. was 5×10^{-6} , and therefore

$$T = \frac{4\pi}{n\Omega} = \frac{4\pi}{1,000 \times 5 \times 10^{-6}} = 2,000 \text{ secs.} = 30 \text{ mins. approx.}$$

This experiment supports the corpuscular conception of radiation for the following reasons: in the first place an accumulation of energy on the bismuth particle must be ruled out on the grounds that the photoelectric phenomenon is instantaneous and that the atoms possess energy levels which are separated from one another; further, one thousand spherical waves originate in the angle 2π , the frequency of the X-rays is of the order of 10^{16} , so that the waves succeed one another at a rate which makes it impossible for one wave alone to give the bismuth particle more than a quantity of energy which is wholly insufficient to expel an electron and the wave-theory does not admit the possibility of the bismuth particle collecting the energy from the whole of a spherical wave (of solid angle 4π). If, on the other hand, the energy consists of light quants which are shot off, when the target is hit an electron is emitted as indicated by calculation from the formula; this electron possesses practically the same energy as the primary electrons from the cathode.

*The Dual Nature of Light as Evidenced by Energy Fluctuations

Wien's formula for the distribution of energy in the spectrum of the black body may be obtained by starting from the conception that radiation is composed of particles of energy $h\nu$; in fact, in Boltzmann's law the density of particles of the class $h\nu$ is proportional to:

$$e^{-W/kT} = e^{-h\nu/kT}.$$

Moreover, this density is also proportional to the number of vibrations of frequencies lying between ν and $(\nu + d\nu)$ and this number is known to be equal to $8\pi\lambda^{-4}d\lambda = (8\pi/c^3)\nu^2 d\nu$,* whence it follows that the specific energy E_ν must be given by

$$E_\nu = (8\pi/c^3)\nu^2 \cdot h\nu \cdot e^{-h\nu/kT}.$$

If, on the other hand, the wave-theory be taken as the basis of the investigation, the formula obtained is that of Rayleigh and Jeans:

$$E_\nu = (8\pi\nu^2/c^3)kT.$$

In 1909 Einstein, in an important paper,† calculated the value of the fluctuations of E ; he investigated the following problem: let us suppose that

* It is known that $E_\lambda d\lambda = E_\nu d\nu$ and, since $\lambda = c/\nu$, $d\lambda = -(c/\nu^2)d\nu$.

† *Phys. Zeits.*, 10, p. 185, 1909.

$$\overline{\epsilon^2} = \int_{-\infty}^{\infty} \epsilon^2 \cdot W \cdot d\epsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Let us begin by calculating ΔS , the increment of entropy of the system, corresponding to a fluctuation ϵ . In consequence of Boltzmann's law (quoted above) the following simple relation holds between ΔS and W :

$$W = (\text{constant}) e^{\Delta S/k} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\Delta S = \frac{\partial S}{\partial E} \epsilon + \frac{1}{2} \frac{\partial^2 S}{\partial E^2} \epsilon^2 + \dots$$

A simple calculation based on the second law of thermodynamics gives :

$$\Delta S = - \frac{\epsilon^2}{2T^2(dE/dT)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\epsilon^2 = kT^2(d\bar{E}/dT) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$
$$\bar{E} = \frac{8\pi\nu^2}{c^3} \cdot \frac{h\nu}{e^{h\nu/kT} - 1} \cdot \nu$$

The value of $d\bar{E}/dT$ thus found, when substituted in (6), gives :

$$\overline{\epsilon^2} = h\nu \cdot \overline{E} + \frac{c^3}{8\pi\nu^2 d\nu} \cdot \frac{\overline{E^2}}{\nu}$$

It is only Planck's law which gives this result.

Let us conclude by considering this equation, applicable to a volume v :

$$\overline{\Delta E^2} = h\nu\overline{E} + \frac{c^3}{8\pi\nu^2 d\nu} \cdot \frac{\overline{E^2}}{\nu} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Let us suppose, on the other hand, that the energy density is extremely small, then formula (1) becomes $\overline{\Delta E^2} = h\nu\overline{E}$, since it reduces to the first term; this, however, is just the value of the fluctuation when the radiation is regarded as being composed solely of light quanta forming a kind of gaseous substance in the enclosure.

The normal condition of affairs is the intermediate case in which there is a

combination of waves and discrete entities (the light quants) ; thus light has what Planck has so expressively termed a Centaur-like nature ; Bohr speaks of the two complementary natures of a single entity.

*The Experiments of Dempster and Batho on Light Quants and Interference *

We have already mentioned the well-known experiments of Wien with canal rays (1924) which led to the conclusion that the time occupied by an atom in emitting radiation as it passed from one state to another was about 10^{-8} seconds ; in particular, Wien finds that the light emitted by the helium atom at the wave-length 4,417 Ångströms diminishes rapidly in accordance with the factor $e^{-2\alpha t}$, where $2\alpha = 5.42 \times 10^7$, so that after 5×10^{-8} sec. the

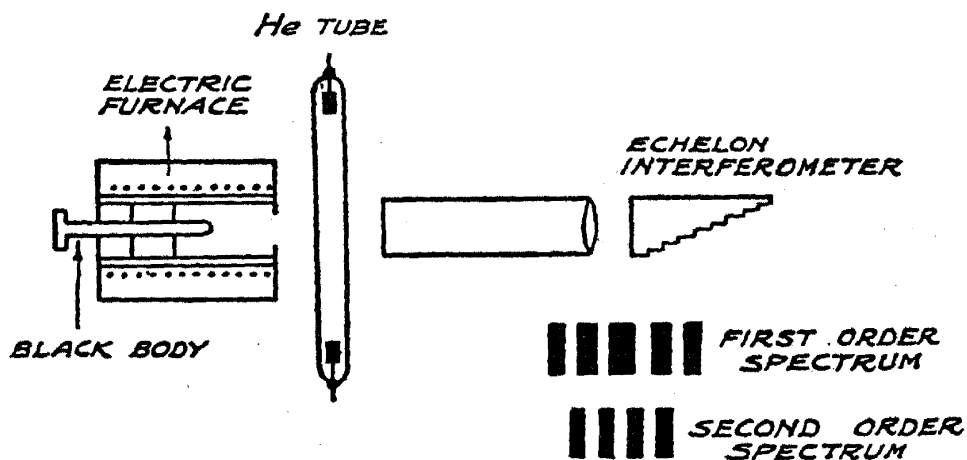


FIG. 57.

intensity has already been reduced to one-fifteenth ; this factor 2α , in fact, expresses the rate of diminution of the active state.

As will be better understood shortly, the idea behind this experiment of Dempster and Batho is to obtain interference fringes with *very feeble light*.

The first of Dempster and Batho's experiments, carried out at the University of Chicago in 1927, had for its object to determine whether the energy in the wave-front *radiated by a single atom* was or was not distributed over the wave-front and the test was made for a solid angle which embraced an area of 32 sq. mm. at a distance of 34 cm. This is the area covered by an échelon spectrometer. A battery supplied a current of about 10^{-15} amp. to a discharge tube

* *Phys. Rev.*, 30, p. 644, 1927. Other experiments of the same kind were carried out by G. I. Taylor in 1909 (*Camb. Phil. Soc. Proc.*, 15, p. 114).

containing helium at low pressure and the energy emitted per second was measured by comparison with that emitted by the black body, F, as will shortly be described.

The light from the helium tube passed first through an échelon grating and then through a prism; the échelon was slightly inclined so as to obtain the spectra of the first and second orders, with their fringes alternated as shown in the figure

With a known current, *e.g.*, $1.2 = 10^{-5}$ amp., photographs of the fringes were taken using an exposure of many hours; the energy was measured by slightly widening the slit through which the emitted light was passed, removing the interferometer and observing whether, at a given temperature, the black body had the same intensity at 4,471 Ång. as the helium tube had at the current used. The comparison was made by using an auxiliary lamp (*i.e.*, a third source) and comparing it in turn with each of the other two.

Now the energy W radiated by an area S of the black body to an area A situated at a distance r from it is given by

$$W = 2E_{\lambda} \cdot S \cdot (A/r^2) \Delta\lambda,$$

in which E_{λ} is given by Planck's formula :

$$E_{\lambda} = hc^2\lambda^{-5} / \{ e^{Nhc/R\lambda T} - 1 \}.$$

A signifies the area of the end of the grating, r is the focal distance of the collimator objective, $\Delta\lambda$ is determined by the width of the slit image. W can thus be found.

Without going into any further details we may say that it was found by this method that 4.2×10^{-10} ergs per second reached the last échelon of the interferometer when the slit was producing a normal series of interference fringes. Since the frequency ν , which corresponds to 4,471 Ång., is known, its quantum has the value 4.41×10^{-12} erg; thus it can be deduced that the energy photographed was only 95 light quants per second. These 95 light quants must have *travelled separately*, since in 5×10^{-18} seconds a light quant vanishes almost entirely.

The conclusion reached by the authors is that a single light quant is capable of producing effects which are due to its

passage through the several steps in the interferometer *simultaneously, i.e.*, that a single light quant must extend over a wave-front which is larger than the solid angle subtended by 32 sq. mm. at a distance of 34 cm. They believed that in this way they had obtained some idea of the size of a light quant.

***Further Consideration of the Experiments of Dempster and Batho. Connection between the Reflected and the Transmitted Portions of a Light Quant.**

It is well known that a thin plate bounded by two parallel planes may give rise to interference fringes by reason of the superposition of (a) the radiation reflected from one of the two surfaces and (b) that which has passed through this surface and has been reflected from the second surface.*

The experimental apparatus used to investigate the reflection of single light quants consisted of a tube of helium at low pressure excited by means of electrons emitted from an incandescent cathode; the light emitted passed through the two parallel planes and produced interference fringes which were examined by means of a spectrograph so that the fringes belonging to each line in the spectrum could be separated.

The volume V of the source producing the fringes was known from the geometry of the apparatus and, by comparison with a black body in the manner described above, the energy radiated at wave-length 4,471 Å. was known for different currents passing through the tube. Actually, when the current was reduced to 10^{-6} amps. or less, the direct comparison was made at the brighter line occurring at 5,016 Å., and the energy in the line 4,471 Å. was deduced from the ratio between the energies in the two lines, this ratio having been established at higher current values.

It was thus possible to obtain a photograph when the source was so feeble that the radiation of wave-length 4,471 emitted in all directions from the volume V was composed of light quants shot out one by one, each dying away before the arrival of its

* Perot and Fabry use a layer of air enclosed between glass plates with a very thin film of silver on each of the two sides facing one another.

successor. The example quoted below * will make the matter clear.

Current in Helium Tube (microamps.).	Time of Exposure.	Volume of Source (mm. ³).	Energy Radiated per sec.	Number of Light Quants per sec.	Probability of Superposition of 2 quants.	Fringes obtained.
I.	II.	III.	IV.	V.	VI.	VII.
0.40	6	1.54	1.54×10^{-5}	3.50×10^6	0.138	distinct
0.10	17	1.54	3.17×10^{-6}	7.21×10^5	0.030	„

The meaning of the first five columns is quite simple ; the sixth column gives the probability that two light quants will overlap ; since a light quant is reduced to one-tenth of its full value in 4.25×10^{-8} sec. (as shown by Wien's observations), we can at once obtain the figures in this column, giving the probability in question.† It will be seen that these are quite small and yet unmistakable fringes are obtained.

The authors conclude that the fringes which are observed must be produced by radiation emitted in an elementary and *simple action* ; this bundle of energy obeys the classical laws of separation at a semi-silvered surface, as required by the wave-theory.

We have described these delicate experiments of Dempster and Batho with some care, and have also stated the conclusion which these authors have drawn from them. Actually, however, the experiments prove nothing, either as regards the dimensions of the quants or as regards the property, ascribed to them, of being able, *each by itself*, to produce interference fringes. Actually these fringes are obtained as the result of exposing a plate for several hours and thus the effect may be the total result, integrated over this period of time, of the quants $h\nu$, the distribution of which over the different parts of the plate is governed by statistical laws.

In other words, whether the light quants arrive crowded together in large numbers during a short space of time, or whether they arrive separately and scattered over a long period, they obey one and the

* A. J. Dempster and H. F. Batho, *Phys. Rev.*, 30, p. 648, 1927.

† It is only necessary to multiply the figures in the fifth column by 4.25×10^{-8} .

same law of distribution ; large numbers of them reach the areas where the bright fringes appear, while comparatively few reach those parts of the screen which show dark fringes.

When *one light quant at a time* passes through the apparatus producing interference, experiment shows that the effect is in no way different from that produced when the intensity is considerable ; the phenomena of interference, then, seem to be absolutely independent of the intensity of the light which produces them.

Maxwell's Theory Gives the Probable Distribution of the Light Quants *

The radiation problem thus assumed the following form : if the atom emits in a discontinuous manner, every emission taking the form of a light quant which carries with it a definite quantity of energy, and if these light quants preserve a real physical identity as demonstrated by their behaviour in the Compton phenomenon, how can their paths be determined by taking into account the equations established by Maxwell ?

The reply to this question emerges from a new conception of the whole problem.

If the luminous intensity is very high, the electromagnetic theory provides a means for calculating exactly both the luminous intensity at different points in space, and the variations produced by the superposition of the waves, variations which agree with those calculated directly from Planck's formula which, in its turn, is based upon and is in accordance with experiment. In the case of very low intensities, however, the formula giving the variations indicates that radiation must be regarded as composed of a collection of discrete particles, but nevertheless the electromagnetic theory—although of a kind which seems quite alien to the problem—enables the distribution of the light quants to be determined whether they be numerous or few. *If, then, we abandon any attempt to determine the path of a single light quant between the moment and the place of its emission, and the moment and place at which it*

* On this subject, see an article by Professor A. Carrelli in *Nuovo Cimento*, April, 1929, Vol. 6, p. XLV.

arrives at the measuring apparatus (the sensitive plate), the electromagnetic theory provides us with the means for determining *the average number of light quants* which reach a given point of an optical system however complicated.

The luminous intensity, then, is simply the probable distribution of the photons.

The necessity for abandoning any attempt to describe the movement of light quants was demonstrated by Heisenberg and by Bohr in critical analyses of the subject which were of fundamental importance.

Heisenberg was the first to formulate (1925), for the range of phenomena involving elementary quantities, a principle which has a number of important consequences ; we shall refer to it at the end of Chap. VIII. The principle is as follows : *No entity should be introduced into physics unless it is possible to devise an experiment, at least of an ideal nature, which will demonstrate the existence of that entity ; no quantity should be introduced unless some means, even if only of an ideal nature, can be devised to measure it.*

In physics, the term *to exist* means to be observable at least as a concept (*i.e.*, ideally), as indicated in the principle just set forth.

Now is it possible to *observe* a light quant, and hence to define its instantaneous position and therefore also its path in space ? It is impossible—and the impossibility is conceptual—to determine the motion of a light quant from a point in space as it travels unchanged away from that point. It is necessary to absorb it, either wholly or partially, in an atom or else to change its path profoundly.*

In the Compton effect, which seems to be adapted to give the instantaneous position of the light quant, what actually happens is that the electron which is struck takes from the light quant a portion of its energy $h\nu$ and converts it into kinetic energy ; this process results in an alteration of frequency and of the direction

* There are certain experiments which cannot be performed practically, but which are not contrary to any law ; these are called *ideal* experiments. Here, however, we are considering an experiment which cannot be performed for theoretical reasons, *i.e.*, one the performance of which it is impossible to *imagine*.

of propagation of the new light quant $h\nu'$; when this effect is completely analysed it is seen to be equivalent to the absorption of the original light quant and the emission of another of lower frequency. No further observation can be made on the original light quant to determine its position.

The physicist who, in the course of his investigations into the nature of light, wishes to know where and how the energy is propagated as it travels on after it has left an emitter and before it has reached an absorber, is in the strange position of not being able to touch the object of his researches without destroying it.

Let us now imagine a perfectly monochromatic plane wave which meets an opaque screen and passes through a small hole cut in the screen; this hole being provided with a shutter. If this shutter be opened and then closed immediately afterwards there is, on the other side of the screen, a small quantity of light which is travelling in the direction of the incident beam. It might seem at first that, by making the hole smaller and smaller, and the time of opening of the shutter shorter and shorter, it would be possible to let through just a single light quant and hence to determine precisely its position at any desired instant. Actually, however, when the hole is very small, the phenomenon of diffraction occurs, the light no longer continues to travel in the direction in which it was incident, so that the velocity is altered by the very process adopted for its determination, and a second determination has no meaning since the quantity is no longer the same. Thus it will be seen that it is meaningless to speak of the path followed by a light quant as one can in the case of a moving body which occupies different positions in space one after another, and which it is possible to observe during its passage without affecting it; this concept is ingrained in us, since it is the result of our continual observation of material bodies; nevertheless, there is no logical reason why it should be equally applicable to radiation.*

Let us consider an atom which emits a single light quant near a photographic plate and let us insert between the atom and the plate an opaque screen with a hole F; we find that a point P on the plate may be affected, although it is not on the line joining

* See an article by Professor E. Persico in *Nuovo Cimento*, July, 1928.

the atom and the hole, or even within the cone defined by the atom (as apex) and the hole (as base).

This is the phenomenon of diffraction. It might be concluded that the light quant did not travel in a straight line. If, now, we cut another hole F' at a suitable position on the screen, so that the difference between the paths SFP , $SF'P$ is half a wavelength (or a multiple of this), the light quant can no longer reach P and the photographic plate is affected at some other point. It may be asked: how does the light quant know what exists, not only on its own path, but also at points remote from its path?

The truth of the matter is that there is no sense in inquiring whether the *photon* has passed through F or F' because we cannot detect any such passage without either destroying or profoundly modifying the phenomenon which is being observed.

To sum up, the optics based on the wave-theory gives us in this case (as in every other complex system involving diffraction, interference, etc.) the intensity distribution at all places where the radiation can be absorbed; to be more precise, it enables us to calculate, for every point in the field, a quantity, I , which is the square of the light vector and which can be interpreted as the *quantity of energy* which falls per second on unit area of a surface; the quantum theory, on the other hand, has so far interpreted I to mean the number of light particles ($h\nu$) per sq. cm. which reach that point per second; actually it only represents the probability that, at that point and in that interval of time, a light quant may be absorbed, as, for instance, by a photographic plate. Thus all the results obtained by means of the classical optics must be interpreted statistically. For a single elementary process of emission it is not possible to speak of the probability of finding a *photon* at any given point. Nor can we regard the energy as propagated by means of waves because this makes it impossible to understand how it can all be collected by an atom in the process of absorption.

When we are no longer observing single elementary phenomena, but their statistical arrangement as in ordinary experiments (Dempster and Batho), we can predict the results with certainty by relying on the law of large numbers.

At this stage in our account of the matter, a gap in the reasoning becomes evident and even a contradiction; the process by which Planck's formula was obtained by Einstein indicated that radiation had a double nature and the fluctuation formula supported this idea, yet in the photo-electric effect, in the Compton effect and, generally, in any interaction between radiation and atoms, the absorption and emission took place in quanta, *i.e.*, discontinuously.

We shall answer this enigma in Chap. VIII; for the present we shall only say that the dilemma presented by these two apparently contradictory ideas is not confined to radiation; in fact, when there was strong evidence that radiation, which had always been thought of as a wave phenomenon, had also a corpuscular character, Louis de Broglie asked whether it was not possible that the electrons, which had hitherto been regarded as corpuscular, might also have the properties of a wave-motion. He showed mathematically* that the dynamics of every particle could be expressed in terms of the propagation of a group of waves, *i.e.*, that a wave-train could be substituted for the particle. The motion of a particle along a straight line is represented by a wave, the wave-length being determined by the momentum mv of the particle in accordance with the equation $\lambda = h/mv$. Thus for light quanta having a momentum $h\nu/c$, the corresponding wave-length is given by $hc/h\nu = c/\nu$, *i.e.*, it is the ordinary electromagnetic wave-length.

Light therefore may still be thought of as propagated by wave-motion; at the same time its energy is concentrated in particles which are connected with this wave-motion, and when light acts it is the particles that come into play. Further, the exact mathematical analysis needed for making the change from the wave to the particle and *vice versa* has now been developed.

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* We shall give an explanation of this argument in Chapter X.

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CHAPTER VII

MAGNETISM AND THE QUANTUM THEORY

Elementary Notions of Magnetic Theory

WEBER, realising that the poles of a magnet can never be separated—breaking the magnet merely increases their number—concluded that a large magnetic mass must consist of a conglomeration of very small elementary magnets. Ampère, observing that there was no essential difference between a magnet and a current, and that free magnetism could never be generated, pictured the elementary magnets of Weber as minute electric currents.

Electric currents we know to be electrons in motion, so that in the last analysis the electron is the fundamental element in magnetism.

Before considering the relation between the quantum of action h and the phenomena of magnetism, it will be useful to give brief explanations of *magnetic moment* and a few other similar notions, for the benefit of any reader for whom these ideas may not be immediately familiar.

The experimental study of the forces exerted on a magnet in a uniform magnetic field shows that these can be reduced to a couple, that is, a system of two equal and parallel forces F acting in opposite senses.

The moment of the couple is the product of the intensity of one of the forces $F = mH$, and the distance b (the arm of the couple). The moment obviously depends on the angle θ between the axis of the magnet and the direction of the field, and equals a maximum when this angle is a right angle.

A magnetic field can, we know, be produced by means of a solenoid consisting of one or more layers of conducting wire wound in a cylindrical spiral. If the solenoid is long, the field in its central part is *uniform*, and proportional to the current strength i and the number of turns of wire n per centimetre length of the solenoid.

The unit of measurement of magnetic field strength is the “gauss.” Expressing the current i in amperes, the magnetic field strength inside the solenoid is given in gauss by the formula :

$$H = 0.4\pi ni.$$

If i is given in c.g.s. units,

$$H = 4\pi ni.$$

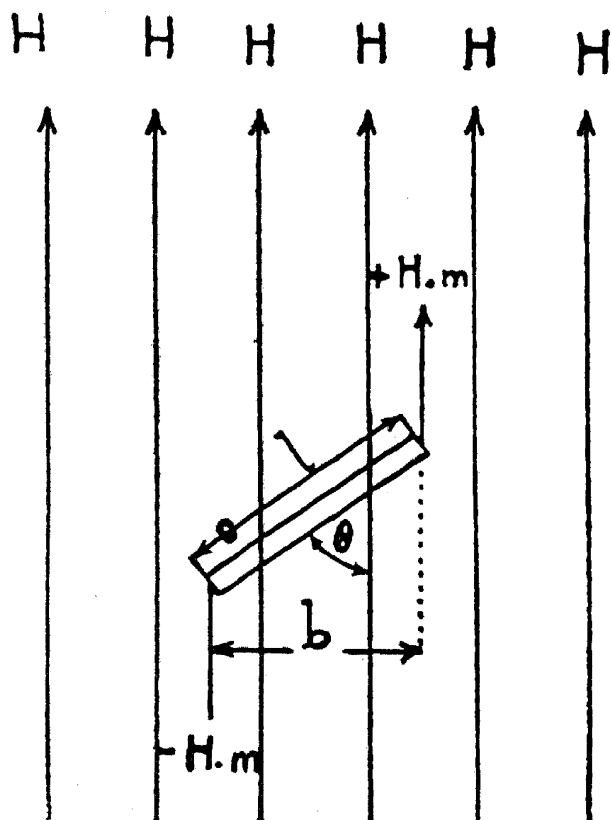


FIG. 58.

The intensity of the earth's magnetic field is equal to a fraction of a gauss. With a solenoid it is easy to produce fields up to one hundred gauss. By means of electromagnets, *i.e.*, solenoids containing iron, fields of some tens of thousand gauss are obtainable.

The magnetic moment of a magnet is determined by the moment of the couple called into play when the magnet is placed, at right angles to the field direction, in a field of one gauss.

The magnetic moment M is given by the product of the pole strength Q and the distance apart of the poles L , $M = QL$. Experiment shows that a magnet can be subdivided into nN small elementary magnets of pole strength $q = \frac{Q}{N}$ and length $l = \frac{L}{n}$ disposed in N parallel rows each containing n elementary magnets. The total moment of the assembly is clearly

$$\begin{aligned} M &= QL = \frac{Q}{N} N \times \frac{L}{n} n = qN \times ln \\ &= nN \times ql. \end{aligned}$$

As (ql) is the magnetic moment of each elementary magnet and nN is their total number, we conclude that the moment of a magnet equals the sum of the moments of the constituent elementary magnets.

The couple acting on a magnet of moment M , inclined at an angle α to the direction of the field H , is given by $MH \sin \alpha$, so that to rotate the magnet through a small angle $d\alpha$ the work required equals $MH \sin \alpha d\alpha$. This expression is obviously the differential with respect to α of the function $W = -MH \cos \alpha$. Changes in W represent work done in overcoming the forces acting on the magnet. The function W is the *potential energy of the magnet in the uniform field*.

A few words in explanation of the repeated references to magnetic moment will not be out of place.

To begin with, "magnetic pole strength" is a fictitious quantity in that whilst a positive or negative electric charge can be isolated and can exist by itself, it is impossible to isolate a magnetic pole, because every such pole is linked with another of opposite character or sign. In fact if a magnet is split up into parts, however small the little magnets so obtained, each will contain equal and opposite poles and the total magnetic "charge" on each will be zero.

We consider a small magnet and its interaction with the external field. This interaction is the same if the original dipole is divided longitudinally and the two parts placed end to end, or if it is divided transversely at the midpoint, and the two halves placed side by side. It is the product magnetic pole strength times length, which counts, and not the pole strength itself.

For example, if in a non-uniform field of gradient $\frac{dH}{dz}$ we introduce a magnet of length dl in the direction of H , the force tending to move the magnet, which is the quantity accessible to experiment, is given by :

$$\text{force} = \frac{dH}{dz} \cdot dl \cdot m = \frac{dH}{dz} \times \text{the magnetic moment}$$

and it is only the moment which has, in effect, a real existence.

To compare the magnetisations of which different substances are susceptible, we must measure the magnetic moments of magnets composed of the respective materials, and refer these moments to unit volume. In this way we arrive at the notion of *intensity of magnetisation*, defined as the magnetic moment per

unit volume. The *specific magnetisation*, on the other hand, is the moment per unit mass. Both magnitudes are *vectors* and have direction and sense in addition to a scalar value. To determine magnetisation it is necessary to specify a vector which has for direction the line joining the poles, in the sense south pole to north pole, and for magnitude, the ratio of the magnetic moment to the volume.

To compare the tendency of different substances to become magnetised, the magnetic moments acquired by equal masses placed in fields of the same intensity are compared. This leads naturally to the definition of the *coefficient of magnetisation (susceptibility)* as the magnetic moment acquired by a gramme of a substance, divided by the intensity of the magnetic field producing the magnetisation.

In the case of iron, matters are more complicated principally because a unique value for the magnetisation corresponding to a given field strength is not obtained. Furthermore, the powerful magnetic poles which appear at the surface of the material give rise in the interior, to a magnetic field which is not in general in the same direction—nor in the same sense—as the external field. The two fields, the demagnetising field and the external field, must be compounded vectorially to give the *total* field and the coefficient of magnetisation is then defined as the magnetic moment of a gramme of material divided by the total field.

By multiplying the coefficient of magnetisation by the molecular weight of the substance we obtain the so-called *molecular coefficient of magnetisation*, the magnetic moment of a gramme molecule divided by the field strength. Finally the value of the coefficient for a single molecule is obtained by dividing this result by Avogadro's number $N = 60.6 \times 10^{22}$. The atomic coefficient is defined in analogous fashion.

The fundamental problem of magnetism is experimental; we have to find for different substances, the manner in which their magnetisations vary with the field strength and with the temperature.

From the point of view of magnetic properties, substances can be classified into three distinct groups: ferromagnetics, paramagnetics and diamagnetics.

The first class comprises iron, magnetite, nickel, cobalt, these substances being characterised by the high magnetisations they can acquire and by the fact that they can become permanent magnets. The magnetisation of paramagnetics is in the same sense as the field and is proportional to the field strength. The coefficients of magnetisation of paramagnetics are very small, to obtain a magnetic moment of one (for unit mass) several hundred thousand gauss being necessary.

Examples of paramagnetics are oxygen, nitrous oxide, ozone, platinum, chromium, manganese, sodium, potassium.

Diamagnetic bodies become magnetised in the opposite direction to the field. Examples: gold, silver, copper, lead, bismuth, water and almost all organic substances. Their coefficients of magnetisation (moment of a gramme in unit field) are of the order 10^{-6} .

The fundamental *experimental laws* governing the magnetic properties of substances were discovered by P. Curie in 1895, and on these the modern theories are based. The most important results of Curie's experiments are summarised in the following statements:—

(1) The susceptibility of diamagnetic substances is independent of temperature.

(2) The susceptibility of paramagnetic substances is in a large number of cases inversely proportional to the absolute temperature,

$$\text{Susceptibility} = \frac{C}{T} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot (\alpha)$$

(3) For other paramagnetic substances, the more general law

$$\text{susceptibility} = \frac{C}{T - \theta} \cdot \cdot \cdot \cdot \cdot \cdot \cdot \cdot (\beta)$$

holds good, where θ is a constant.

(4) Ferromagnetism decreases as the substance is heated up, vanishing altogether at a particular temperature termed the *Curie point*. Above the Curie point, the substance is merely paramagnetic and follows the (β) law with θ set equal to the Curie point temperature.

Diamagnetism

The experimental study of diamagnetism has established that the coefficient of magnetisation C_d is almost independent of temperature, as Curie showed in 1895. This result has been verified for a large number of metals, metalloids and organic compounds over very wide temperature ranges. For arsenic in the range -200° to $+200^\circ$, $C_d = -0.3 \times 10^{-6}$. For hydrogen gas, $C_d = -2 \times 10^{-6}$.

We shall see below how, by measuring the coefficient of magnetisation C_d , an approximate value for the atomic radius can be found.

If the orbit of an electron rotating about a nucleus encloses an area S the electron gives rise to a magnetic moment of amount $S \times e \times n$, where n is the number of revolutions described per second. The motion of the electron, taken as a whole, is equivalent to a current. If the orbits contained in an atom form a rigid system, their moments can be compounded. It may happen that the orbits are so arranged that the resultant atomic moment is zero, or it may be different from zero. In the latter case, in the absence of an external field, the directions of the atomic moments will be distributed at random and the resultant moment of a volume element of the substance containing many atoms will be zero. An applied field tends to make the magnetic axes parallel, and a resultant moment in the *same sense* as the applied field is developed. Thus the substance as such is paramagnetic.

It will, however, be shown immediately that, for this case as well as for the other alternative—when the atomic moment is equal to zero—the substance will nevertheless appear diamagnetic,

and if it does not the reason is that the paramagnetism originating, in the way described above, masks the diamagnetism.

For simplicity, consider a single electron describing a circular orbit with the applied magnetic field H perpendicular to the plane of the orbit. Denoting the angular velocity by ω , the radius by r and the electronic mass by m , the centrifugal force is given by $m\omega^2 r$. The effect of the magnetic field is merely to accelerate

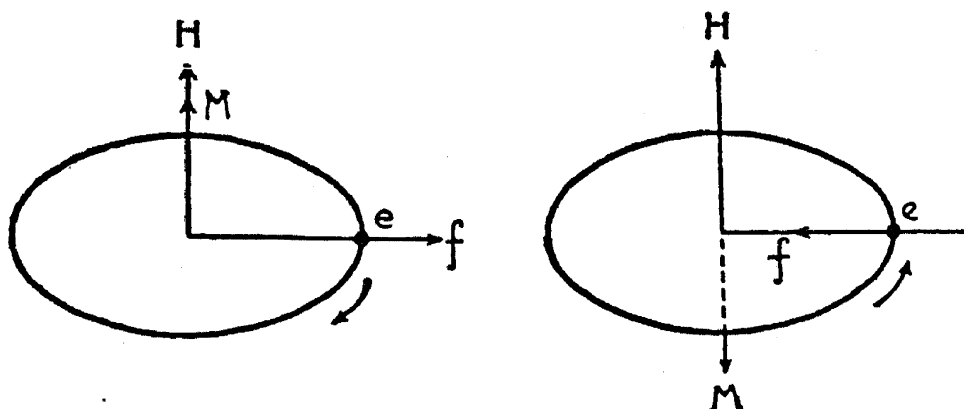


FIG. 59.

or retard the electron in its orbit without changing the radius. Thus we may write,

$$F - He\omega r = m(\omega + \Delta\omega)^2 r \quad \text{where } F = m\omega^2 r.$$

In this equation the left hand side represents the total applied force on the electron, the right hand side, the modified centrifugal force.

Supposing $\Delta\omega$ small compared with ω , it follows that,

$$\Delta\omega = -\frac{He}{2m},$$

and the magnetic moment due to this increase of angular velocity is given by :

$$\Delta M = \text{area described} \times e \times n = \text{area} \times e \times \frac{\Delta\omega}{2\pi} = -r^2 \frac{He^2}{4m}. \quad (1)$$

The sense of this additional moment is *always opposite to that of the field* H , whether the electron moves in its orbit in the clockwise or anti-clockwise sense. This is so because reversing the direction of motion of the electron in its orbit, also reverses the direction of the Laplace force acting on it.

Thus on applying a field H the total moment of the atom, the resultant of the partial moments due to the various electron orbits, varies in the same way, whether the initial atomic moment is zero or not. All substances should therefore appear diamagnetic if it were not for the fact that the paramagnetic behaviour of the atom as a whole may mask the diamagnetic effect, which is always extremely small even in very strong fields.

In an atom of atomic number Z there are Z electrons and therefore Z orbits to consider. The change of magnetic moment ΔM referred to a gramme atom, is equal to ZN multiplied by the value for a single atom containing a single circular orbit, given in (1). If the orbits are not all identical circular orbits, in summing their effects it will be necessary to replace r^2 by a suitable mean value R^2 .

For an orbit inclined at an angle α to the direction of the field H the change of magnetic moment is given by :

$$\Delta M = - \frac{e^2 H r^2 \cos \alpha}{4m} \quad \dots \dots \dots (2)$$

Resolving the vector ΔM in the direction of H introduces a further factor $\cos \alpha$, so that in averaging over all values of $\cos \alpha$ the mean value of $\cos^2 \alpha$ is required. The appropriate mean value of $\cos^2 \alpha$ is $\frac{1}{3}$, so that we have finally for the total magnetic moment per gramme atom :

$$- \frac{e^2 H N Z (\pi R^2)}{4\pi m} \frac{2}{3} = - \frac{1}{6} \frac{e^2 H N Z (\pi R^2)}{\pi m},$$

where πR^2 represents the average orbital area. The susceptibility is then given by :

$$C_d = - \frac{1}{6} \frac{e}{m} \cdot Z N e R^2 \quad \dots \dots \dots (3)$$

Ne is the charge of a gramme ion as observed in electrolysis ($Ne = 9,650$ electromagnetic units); $\frac{e}{m}$ is the ratio of the charge to the mass of an electron and has the value 1.77×10^7 . Hence

we derive from equation (3) the following expression for the mean square of the radius of the atom :

$$R^2 = -0.35 \times 10^{-10} \times \frac{C_d}{Z}.$$

C_d = susceptibility.

Z = the atomic number, or the ordinal number in the Mendeleieff classification.

Applying this expression to a few actual cases we obtain the accompanying table :

	Z	C_d	R (calculated).
Helium . . .	2	-1.90×10^{-6}	0.57×10^{-8} cm.
Nitrogen . . .	7	-6.0 „	0.55 „
Copper . . .	29	-18 „	0.47 „
Silver . . .	47	-31 „	0.48 „

It is clear that the atomic radii calculated in this way are of the same order of magnitude (about 10^{-8} cm.) as the values derived from kinetic theory. Actually, the present method gives in each case a rather lower value. This can be accounted for by our use of the mean value, R^2 . For heavy atoms, such as silver, lead, etc., of high atomic number, many of the orbits are situated deep in the interior of the atom, and the mean value R must necessarily be smaller than the radius given by kinetic theory.

The idea that magnetism originates in the motion of electrons about the nucleus might be given up. It in no way affects the determination of the magnetic moment of the atom, in so far as this results from the applied field, whether or not the trajectory of the electron gives rise to a magnetic moment. In abandoning the *mechanical* picture of the atom, however, that which in diamagnetism appears as a splitting apart of the atom, becomes a new definition of the magnitude of the diamagnetic effect.

A final observation about diamagnetism and we pass on to consider paramagnetism.

By plotting the ratio of susceptibility to atomic number, as ordinate, against atomic number as abscissa, a graph is obtained

which exhibits a well-marked periodicity (see Fig. 60). There will of course be gaps in the diagram corresponding to the paramagnetic and ferromagnetic elements, which separate the diamagnetic substances into discontinuous groups. The close relationship between elements in the same column of the periodic table is clearly brought out.

Temperature has no effect on diamagnetism. The temperature

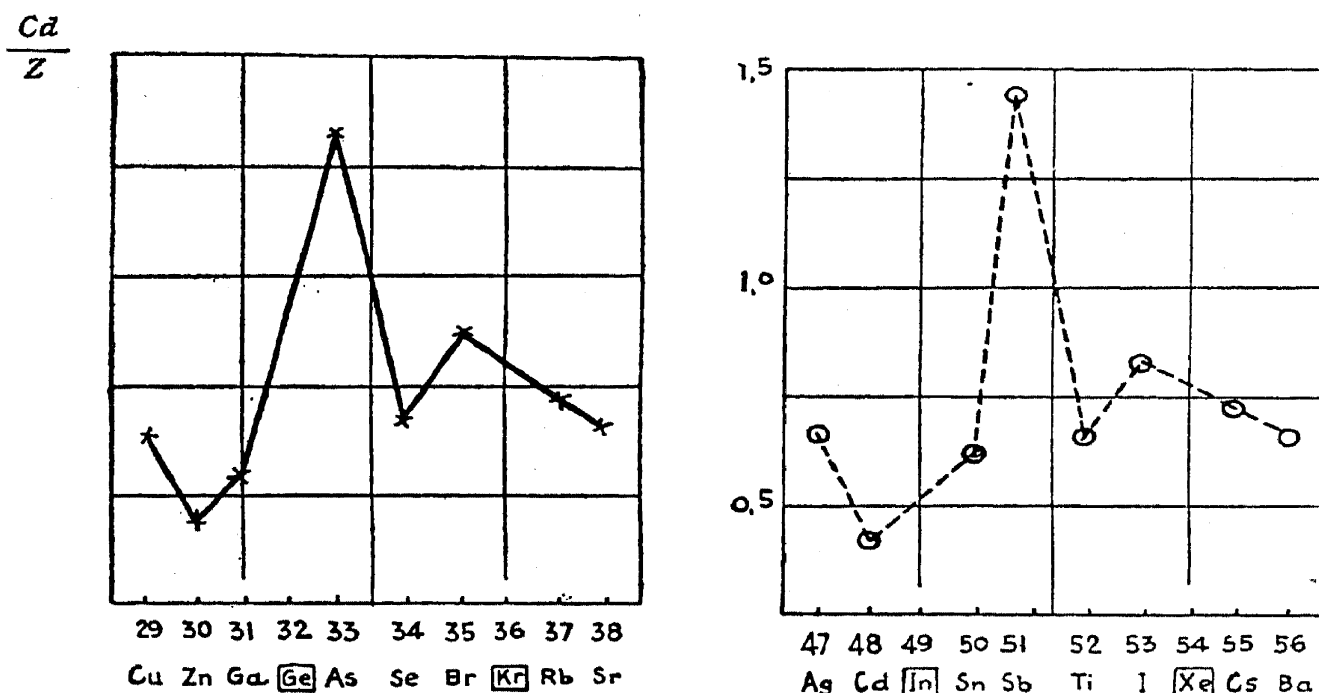


FIG. 60.

of a body is the net result of the disorganised motion of the *molecules*, and the rapid movements of the electrons in the interior of the atoms are unaffected by the molecular motion.

Paramagnetism, on the other hand, is a molecular property and depends on the temperature. It varies directly as the intensity of the external field and inversely as the absolute temperature.

Paramagnetism of Perfect Gases and Dilute Solutions. Langevin's Law

For paramagnetic substances the susceptibility $\frac{\sigma}{H}$, the ratio of the moment of unit mass to the field strength, is in general very small, of the order of a millionth. For salts of iron and of manganese it is somewhat larger, of the order 10^{-4} .

When the molecules are widely separated so that they exert no appreciable orientating action one on another, as in perfect gases or dilute solutions, the magnetisation σ varies inversely as the absolute temperature, and we can write $\sigma = C \frac{H}{T}$ where the constant C is known as the Curie constant, after the discoverer of the law.

As an example, we may mention the magnetisation of oxygen, which has been examined at ordinary temperatures in fields of from 100 to 20,000 gauss and at pressures ranging from 1 to 100 atmospheres. For the ratio $\frac{\sigma T}{H}$ the same value 104×10^{-6} was always obtained. At other temperatures the constancy of the ratio $\frac{\sigma T}{H}$ was also exactly verified.

The same law holds for dilute solutions of paramagnetic salts, which exist in a state analogous to that of gases, the ions, the carriers of the magnetic moments, moving about in the solvent independently of each other. Naturally, for solutions, the law can be verified only within restricted temperature limits determined by changes of state of the solvent (vaporisation or solidification).

The theory of paramagnetism correlating the observed susceptibilities with molecular data was given by Langevin in 1905, and we reproduce it here in brief, noting, however, that it has since been subjected to revision.

In the absence of the magnetic field H the magnetic axes of the molecules of a gas are distributed in all directions at random. The sum of the projections of the elementary moments on any straight line is zero. If, however, we suppose a magnetic field to be applied, and imagine the thermal agitation of the molecules eliminated in some way, then all the elementary magnets will swing round until their axes lie along the direction of the applied field, and the gas will possess the greatest magnetisation of which it is capable, σ_0 . Finally, if both the field and the thermal agitation function together, as in the actual case, a magnetisation of the gas will be observed which increases with the field and decreases with rise of temperature. The law relating the observed

magnetisation σ and the two variables of the problem, the field H and the absolute temperature T , was derived by Langevin in the following manner.

A molecule of gas is a small magnet which, when placed in a field of strength H with its magnetic axis inclined at an angle α to the direction of the field, possesses potential energy of amount :

$$w = -\mu H \cos \alpha,$$

where μ denotes the molecular magnetic moment. Boltzmann's celebrated theorem, which we have already encountered in the kinetic theory of gases, determines the statistical distribution of the molecules and tells us how many there are which in the field take up each particular orientation. Expressed more exactly, given N molecules the number of these inclined at an angle α to the field direction, is *proportional* to :

$$\frac{Nw}{e^{RT}} = e^{\frac{-N\mu H \cos \alpha}{RT}},$$

R = the perfect gas constant, N = Avogadro's number.

The *distribution* of the molecules being known, so also is that of the elementary magnetic moments whose projections on the field direction when combined furnish the total moment of unit mass, *i.e.*, the magnetisation σ which is observed experimentally.

The contributions of the elementary magnets must be summed or integrated, a simple problem of calculation,* of which we shall

* The details of the calculation are as follows : The number dn of molecules with axes in the solid angle $d\omega$ making an angle α with the field direction, is given by,

$$dn = Ke^{-\frac{N\mu H \cos \alpha}{RT}} d\omega \quad \dots \quad (K \text{ is a constant}) \quad (1)$$

$d\omega$ is the solid angle corresponding to the plane angle $d\alpha$ so that $d\omega = 2\pi \sin \alpha d\alpha$. Inserting this value in (1) we have,

$$dn = Ke^{-\frac{N\mu H \cos \alpha}{RT}} 2\pi \sin \alpha d\alpha \quad \dots \quad (2)$$

where α varies from zero to π .

If the volume under consideration is a sphere containing one gramme molecule of the gas, we must have $\int dn = N$, and this condition determines the value of the constant K .

It merely remains to sum up the components of the elementary magnetic moments resolved in the direction of the field. A group of dn molecules

at once give the result. The sum of the components of the magnetic moments in the direction of the field, for all the molecules in unit mass is found to be :

$$\sigma = \mu N \left[\frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \right]$$

where $a = \frac{\mu H}{RT}$. As μN is the saturation value σ_0 we may write :

$$\sigma = \sigma_0 L(a),$$

where $L(a)$ denotes the rather complicated "Langevin function."

The quantity σ_0 is a constant characteristic of the gas and is the magnetisation which would be acquired by unit mass of the gas if all the elementary magnetic moments were lined up parallel to the field direction. It always exceeds σ . In dilute solutions of salts, for molecule is to be understood the quantity of matter which corresponds to a gramme atom of the carrier of the magnetic moment. For example, ferrous sulphate FeSO_4 contains one atom of iron whereas ferric sulphate $\text{Fe}_2(\text{SO}_4)_3$ contains two, and the effective gramme molecule for paramagnetic effects in the latter case is only one-half the gramme molecule as usually defined.

Thus we have arrived at the complete expression for the magnetisation σ as a function of the field strength and the temperature. Expanding the exponentials e^a , e^{-a} in powers of a we obtain,

$$\frac{\sigma}{\sigma_0} = \frac{a}{3} - \frac{1}{45} a^3 + \frac{2}{945} a^5 - \dots \dots \dots (5)$$

and for fairly small values of a (lying between 0 and 0.4) the error

contributes a magnetic moment $\mu \cos \alpha dn$ and the total moment of unit mass is given by the integral

$$\sigma = \int_0^\pi \mu \cos \alpha dn \dots \dots \dots (3)$$

Substituting for dn from (2) above, evaluation of the integral leads to

$$\sigma = \mu N \left(\frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \right)$$

where $a = \frac{\mu H}{RT}$ and K has been eliminated by the aid of the relation $N = \int dn$

or $N = \frac{2\pi K}{a} (e^a - e^{-a})$.

due to neglecting all terms beyond the first, is less than one per cent. It then follows that :

$$\frac{\sigma}{\sigma_0} = \frac{a}{3}, \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (6)$$

a simple and extremely important result.

In Fig. 61 Langevin's celebrated curve representing the law (5) is reproduced. It is seen from the figure that the initial part of the curve is sensibly linear corresponding to the equation (6).

In practice it may happen that, a being small, it is sufficient to consider merely the initial linear part of the Langevin curve. For

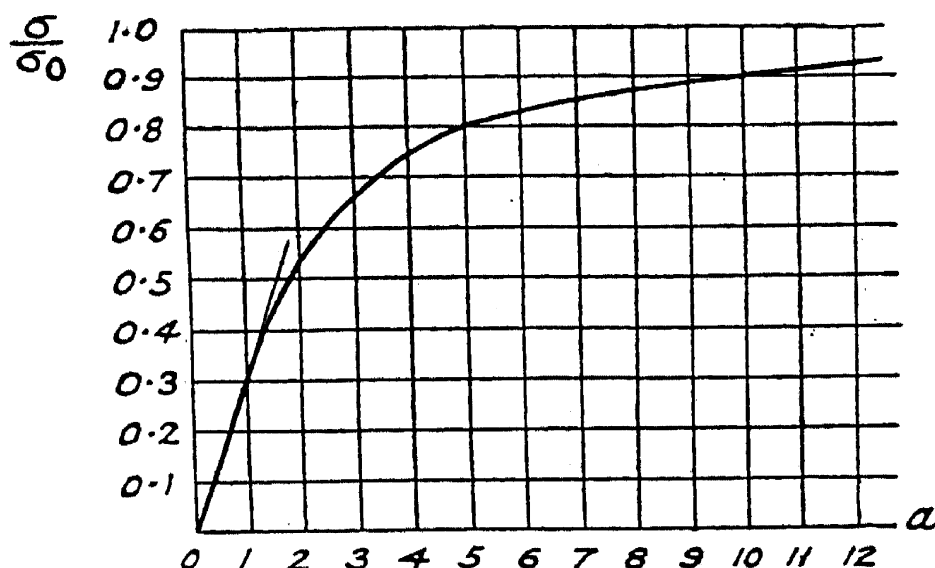


FIG. 61.

highly magnetic substances, such as the manganese salts, μ equals

$$\frac{32,800}{N} = \frac{32,800}{60.6 \times 10^{22}}, \quad 32,800 \text{ being the magnetic moment per}$$

gramme atom of Mn in the manganese salts. At ordinary temperatures T is about 290° and R the perfect gas constant equals 8.315×10^7 . It follows that even for powerful fields (say,

20,000 gauss) at ordinary temperatures $a = \frac{\mu H}{RT}$ will always be so

small that the simple formula $\frac{\sigma}{\sigma_0} = \frac{a}{3}$ is sufficiently exact. Only at very low temperatures near to the absolute zero (at 1° say, a temperature attainable with liquid helium), will it be possible to experiment on the non-linear portion of the Langevin curve and

test the theory. Unfortunately, at such low temperatures, all the paramagnetic gases, including oxygen, pass into the solid state and the same difficulty applies in the case of dilute solutions of salts.

No substances being available in which the magnetic molecules are free, the theory has been tested for a solid substance, gadolinium sulphate, which conforms to Curie's law. For temperatures between 1.3° and 20° absolute, the ratio $\frac{\sigma}{\sigma_0}$ and the

corresponding value $a = \frac{\mu H}{RT}$ were determined, for fields up to 22,000 gauss. Plotting $\frac{\sigma}{\sigma_0}$ as ordinate against a an abscissa, the *Langevin curve was reproduced*. The method for determining σ_0 , and hence μ , from these experiments will be explained in the next section.

Derivation of the Atomic Moment and the Absolute Saturation, from the Experimental Data

The absolute saturation σ_0 (which refers to unit mass) and the moment of an atom μ , are related by the simple equation :

$$\mu N = \sigma_0 m \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where m is the molecular weight, so that knowing σ_0 , μ can be determined. To obtain σ_0 we observe that, omitting the extreme case in which the temperature approaches the absolute zero and the field is very powerful, the law of paramagnetism reduces to the simple form :

$$\sigma = \sigma_0 \frac{a}{3} = \sigma_0 \frac{\mu N H}{3RT},$$

or, substituting from (7),

$$\sigma = \frac{m \sigma_0^2 H}{3R T}.$$

Comparing this expression with the Curie law $\sigma = C \frac{H}{T}$, it is evident that the Curie constant C is connected with the absolute saturation by the equation :

$$C = \frac{m \sigma_0^2}{3R} \quad \text{or} \quad \sigma_0 = \sqrt{\frac{3RC}{m}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Here σ_0 is the moment per unit mass, so that the Curie constant must also refer to unit mass. The saturation moment of the *gramme atom* will be m times as large, namely,

$$\text{Moment of the gramme atom} \quad M = \sqrt{3RCm}; \quad . \quad . \quad . \quad (9)$$

m is the magnetic gramme molecule, in other words, the quantity of matter containing a paramagnetic gramme atom free to orientate itself.

If the Curie constant is referred to the gramme molecule (or gramme atom which is the same thing) the simpler formula :

$$C = \frac{M^2}{3R} = \frac{\mu^2 N^2}{3R} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9^1)$$

is obtained.

The above explanations show how, knowing the Curie constant,

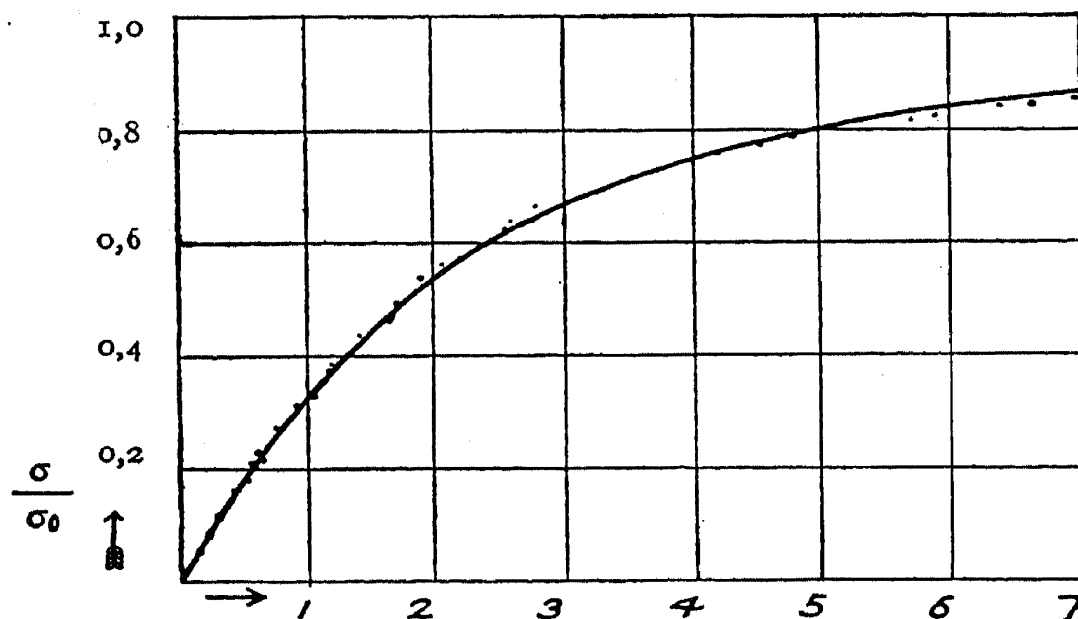


FIG. 62.

the absolute saturation σ_0 and the moment of the atom μ can be determined from the formulæ (8) and (7) respectively. Formula (9) is important as the principal source of atomic moments.

In the preceding section, in discussing the verification of Langevin's theory in the case of gadolinium sulphate

$\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, $\frac{\sigma}{\sigma_0}$ as ordinate was plotted against a as abscissa (see Fig. 62). σ is given by the experiment itself. We have just seen how the saturation value σ_0 is obtainable from the

Curie constant, and from this can be derived the atomic moment μ which is required to form the expression a .*

We shall see on p. 256 that Langevin's theory and equation (9) must be modified. Here again it is found that the principles of classical mechanics cannot be applied in their entirety, to atomic and molecular phenomena.

Paramagnetic Substances with Molecular Field. Theory of Weiss

In discussing paramagnetic substances and Curie's law $\sigma = C \frac{H}{T}$, to which they conform, it has been stated that the molecules of these substances—gases and dilute solutions—are free to orientate themselves like the molecules of a perfect gas, opposing no resistance to the turning action of the external magnetic field except that due to the disorganising effect of thermal agitation. If, however, the molecules are mutually influenced by their elementary magnetic moments, the substance no longer obeys Curie's law.

For this class of substances Weiss has elaborated a theory which takes account of many of the facts and we shall just mention the initial steps involved in his work. Weiss assumes that in a magnetised body the action of all the molecules possessing magnetic moment, on one such molecule, is equivalent to a magnetic field proportional to, and in the same direction as the magnetisation σ . This field, termed the *molecular field*, has the value $H_m = n\sigma$ ($n = \text{a constant}$), the magnetisation itself being a function of the *total field*,

$$H + H_m = H + n\sigma.$$

The molecular field was originally introduced to explain the behaviour of ferromagnetic substances, but it is known that the forces included in the molecular field are not necessarily of magnetic origin and are more probably electrical in character.

* The observational curve tends towards a saturation value and the final points are not more than about 16 per cent. lower than the maximum calculated from Curie's constant. Thus the saturation value to which the curve tends, and which corresponds to complete parallelism of the elementary magnets, agrees with that derived from Curie's constant.

Curie's law remains applicable in the modified form

$$\sigma = C \frac{H + H_m}{T} = C \frac{H + n\sigma}{T} \quad \dots \quad (1)$$

The susceptibility,

$$\frac{\sigma}{H} = \frac{C}{T - Cn} \quad \dots \quad (2)$$

becomes infinite at a particular temperature $\theta = Cn$ which is termed the *Curie point*.

As examples of this class of substances may be mentioned concentrated solutions of certain salts of iron, cobalt and manganese studied by Foex (1921), and oxygen gas under high pressure.*

Ferromagnetic substances (certain metals and alloys) at temperatures higher than the Curie point obey the law,

$$\frac{\sigma}{H} (T - \theta) = C.$$

At the Curie point their intense spontaneous magnetisation disappears, and at higher temperatures the magnetisation becomes proportional to the field strength.

Determination of Atomic Moments. The Bohr Magneton

Up to this point we have given a simple treatment of the statistical side of magnetism, showing how the magnetic properties

* Oxygen which at pressures below 100 atmospheres conforms, as we have seen, to the simple law $\sigma = C \frac{H}{T}$, at higher pressures gives evidence of a molecular field. Experiments by Kamerlingh-Onnes on compressed oxygen of density 0.15, at temperatures between 147° and 249° absolute, have shown that the expression $\frac{H}{\sigma} (T + 5.4)$ is constant, *i.e.*, compressed oxygen obeys the law (2) and the Curie point is actually 5.4° *below* the absolute zero. This is in no sense an impossible result. It simply means that the line representing the relation between $\frac{H}{\sigma}$ (the reciprocal of the susceptibility) and the absolute temperature, fails to pass through the origin of co-ordinates. We know that the value of $C = \frac{\sigma}{H} (T + 5.4)$ should coincide with the Curie constant obtained for oxygen gas at ordinary temperatures by inserting the measured values of σ , H , and T in the expression $\sigma = C \frac{H}{T}$. This is in fact verified by the experiments.

of matter in bulk originate from the elementary magnetic moments. Nothing has yet been said about the unit of magnetic moment which plays a fundamental part in this important, and until a few years ago obscure, branch of physics.

Just as the electron is the unit of electricity, so the magneton is the unit of magnetic moment. As, however, an electron moving round in an orbit constitutes a minute magnet, it is clear that the new unit will depend on the electron, and, in the final analysis, will be expressible in terms of the elementary electric charge. Consider the simplest atom, the atom of hydrogen with its single electron moving round in an orbit of known radius and velocity determined by the Bohr condition. All the quantities required to determine the unit of magnetic moment are here fixed, and it remains only to carry out the calculation.

Let ω and a be respectively the angular velocity of the electron and the radius of the orbit. The strength of the current corresponding to the moving electron is, by definition, the quantity of electricity traversing a section of the circuit in unit time, and this is obviously given by $\frac{e\omega}{2\pi}$. The elementary magnetic moment μ of the circuit of area πa^2 then becomes :

$$\mu = \frac{e\omega}{2\pi} \cdot \pi a^2 = \frac{e}{2} \omega a^2 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

By the quantum theory, the radius a is not arbitrary, but must have one of a series of *discrete* values determined by the condition :

$$m_0 \omega a^2 = \frac{nh}{2\pi} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where n is an integer.

Hence, eliminating ωa^2 from (1) and (2),

$$\mu = \frac{e}{m_0} \frac{nh}{4\pi} \quad \text{with } n = 1, 2, 3, \dots$$

The smallest elementary moment, the unit of magnetic moment, is obtained by putting $n = 1$. Multiplication by Avogadro's number gives the corresponding magnitude for the gramme atom.

Fundamental unit of magnetic moment, termed the magneton

$$\mu_0 = \frac{e}{m_0} \frac{h}{4\pi}.$$

It should be observed that *mechanical magnitudes* have disappeared from the result. Inserting the numerical values $\frac{e}{m_0} = \frac{5.30 \times 10^{17}}{3 \times 10^{10}}$, $h = 6.55 \times 10^{-27}$, we obtain for the Bohr magneton, so-called in honour of the great Danish physicist,

$$\text{one Bohr magneton} = 0.91 \times 10^{-20} \text{ c.g.s. units,}$$

or, multiplying by Avogadro's number, 5,560 gauss \times cm. per gramme molecule.

We have considered only a single orbit, but in any other atom, to each orbit corresponds an elementary moment and these moments add up geometrically to give the total moment; in other words, one takes the sum of the projections of all the individual moments on the moment axis. These projections of the vectors $\frac{e}{m_0} \frac{nh}{4\pi}$ are all multiples of $\frac{e}{m_0} \frac{h}{4\pi}$, for we have seen on p. 124 that a moment fixed by the azimuthal quantum number n , when projected on to a *fixed axis*, again gives an integral moment, and the direction of the external field is to be taken as the axis of projection.

It appears at first sight, therefore, that the observed magnetic moments should be multiples of the Bohr magneton. In reality they are much more complex, because the atom, in addition to the magnetic moment due to the orbital motion of the electrons, possesses also another magnetic moment which is the resultant of moments associated with the electrons themselves. We shall see, however, that the magneton theory is in fact valid and the magneton is obtained experimentally with the value just calculated.

As regards the practical determinations of the moments of the atom, we shall explain a little later the method introduced by Gerlach and Stern, which forms at the same time, a remarkable confirmation of the quantum theory. In practice two other procedures may be utilised. For a ferromagnetic substance, the

susceptibility is measured at a very low temperature and in a powerful field, so that absolute saturation is approached. Extrapolating to $H = \text{infinity}$, $T = 0$ and multiplying the result by the atomic mass gives the atomic moment.

For paramagnetic substances the atomic moment is calculated from Curie's constant, using the relation,

$$\text{moment of the gramme atom} = \sqrt{3RC}.$$

It should be observed that Langevin's result rests on certain hypotheses, on the continuously variable orientation of the magnetic axes of the particles with respect to the field direction, on the validity of Maxwell's statistical law, on the structure of the atom and the relation between magnetic and thermal energy (the assumed smallness of the ratio $\frac{\mu H}{RT}$). In the arbitrary character of these hypotheses lies the uncertainty in calculations of μ by the Langevin formula.

In the case of solutions, the observed magnetisation must also be corrected for the diamagnetism of the solvent and of the chemical radical combined with the paramagnetic atom. For example, in nickel sulphate the diamagnetism of the SO_4 radical calls for a correction to the apparent atomic moment of nickel amounting to 0.37 per cent.

The experiments of Kamerlingh-Onnes on gadolinium sulphate furnish the sole example of an atomic moment determined by both methods, measurement of the saturation magnetisation at low temperatures and calculation from Curie's constant. The two determinations agree. In solid substances, however, the atomic moments have not the freedom to orientate which, as we saw on p. 123, results in *spatial quantisation*.

Gerlach and Stern's Experiments,* confirming the Intervention of Quantum Theory into Magnetism.

We have seen that the magnetic moment M generated by an electron moving in an orbit, circular or otherwise, is equal to

* *Zeits. f. Physik*, 7, p. 249; 8, p. 100; 9, p. 349, 1922. *Ann. d. Phys.*, 74, p. 673, 1924; 76, p. 163, 1925.

$M = \frac{h}{4\pi} \frac{en}{m_0}$, where n is the azimuthal quantum number, and that the unit of magnetic moments is the so-called :

$$\text{Bohr magneton} = \frac{h}{4\pi} \frac{e}{m_0}.$$

In the presence of a magnetic field the atomic moment cannot point in any direction whatever, but must instead be orientated in such a way that its projection on the field direction is an integral multiple of the Bohr magneton. We recall that if an electron is describing an orbit of quantum number n the corresponding magnetic moment can be inclined to the field direction only at the angles given by the formulæ :

$$\cos \alpha_1 = \pm \frac{n}{n}, \text{ that is, } \pm 1$$

$$\cos \alpha_2 = \pm \frac{n-1}{n},$$

$$\cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot$$

$$\cos \alpha_n = \pm \frac{1}{n}.$$

In the particular case of the orbit with $n = 1$ the moment is one Bohr magneton, and only the two directions $\cos \alpha = \pm 1$, i.e., $\alpha = 0$ or $\alpha = \pi$ are possible. The possible directions are thus reduced to parallelism with the field, in the same and in the opposite sense.

It is this important deduction from the quantum theory that Gerlach and Stern (1921) subjected to experimental confirmation. At the same time they were able to verify the theoretical value of the Bohr magneton as actually existing in the atoms of silver and other elements.

Referring to Fig. 63, F represents an electrically-heated oven in which a high vacuum can be maintained. The oven is filled with an atmosphere of silver vapour by heating a fragment of the metal, placed inside, to a temperature of about 100°C . above the melting point. The atoms of silver vapour escape by way of the aperture A and pass through the two diaphragms $S_1 S_1$ and $S_2 S_2$,

forming a narrow pencil of "rays," * in which the atoms travel forward with the velocity of their thermal motion.

The rays then pass between the poles P_1 , P_2 of an electromagnet, one of the poles, P_1 , being cut to form an edge, as shown in section in the right-hand sketch of Fig. 63. The beam of atoms moves along parallel to the edge at a distance of some tenths of a millimetre, and impinges on a suitably-placed photographic plate. The whole apparatus is contained in a vessel in which a high vacuum is maintained.

The magnetic field tends to draw towards the edge those atoms which have their magnetic moments pointing in the same direction

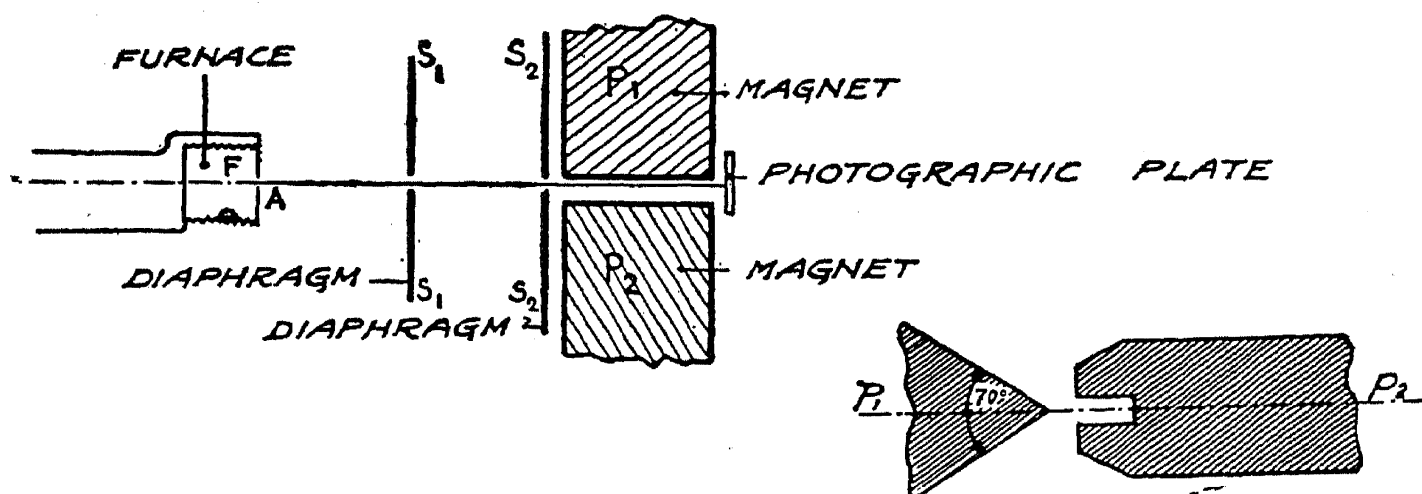


FIG. 63.

as the field. Atoms with magnetic moments in the opposite direction are driven away from the edge. These forces are due to the non-uniformity of the magnetic field, which is very pronounced in the neighbourhood of the edge. Finally, the atoms strike the photographic plate and stick there, but owing to the small quantity of matter deposited no visible trace is obtained until the plate is developed.

On carrying out the experiment, in the absence of magnetic field a sharply-defined spot is obtained at the point where the straight line pencil of rays passing through the diaphragms strikes the plate.

Consider now what we might expect to happen when the magnetic field is applied. The atoms travel with different

* Molecular rays were obtained for the first time by Dunoyer.

velocities and all orientations of atomic moments are equally represented in the beam. This should hold good in spite of the magnetic field because, although the atoms are subject to the Larmor precession, this does not alter the average distribution of their axes in space. At the most the weak paramagnetism of the gas will result in a slight excess of atoms turned with their axes along the field as against those turned in the opposite direction. It would appear therefore that we should obtain on the plate a spot drawn out along the direction of the field, with its maximum intensity at the position of the undeviated ray.

On the other hand, if quantum theory considerations hold good, the narrow pencil of atoms should be split into two distinct parts containing atoms orientated respectively in the same direction as the field, and in the opposite direction. No single atom should move along the straight line trajectory of the undeviated ray. Experiment confirms completely this striking prediction of the quantum theory. Two spots are obtained, displaced in opposite directions along the line, and careful observations establish the entire absence of deposit at the position of the undeviated ray. Moreover, knowing the field strength and its gradient, the velocity of the atoms, and the length of the edge along which the displacing forces are in operation, the deviation is calculable. Conversely from the observed value of the latter, the magnetic moment can be deduced.

Gerlach and Stern found complete agreement between the observed deviations and those calculated, assuming the silver atom to have a magnetic moment of one Bohr magneton. The experiments were repeated (1924), using copper and gold, and the same value for the atomic moment—one Bohr magneton—was obtained.*

Lead, tin, zinc, cadmium and mercury all give atomic rays which are not deflected by the magnetic field. Thus the atoms of these elements do not carry a magnetic moment. Bismuth gives a ray deviated by a considerable amount towards the pole

* Considerable care is necessary in drawing conclusions from these experiments, as the atomic rays contain atoms of all possible velocities and the deviation increases with decrease in velocity.

edge, and an undeflected ray indicating the presence of atoms of zero magnetic moment. Thallium shows a small moment of $\frac{1}{3}$ of a magneton.

This quantitative confirmation of the theoretical value of the Bohr magneton must be accepted as one of the outstanding successes of the quantum theory.

We cannot stay to give a detailed analysis of the results. We merely mention that they are in excellent agreement with our present views on atomic structure, and can be interpreted, using our knowledge of multiplets and the now completed theory of the anomalous Zeeman effect in which the magnitude of the separation is obtained from the splitting factor g (see p. 135).

For silver, as for the alkalis, the *fundamental term* * corresponds to $m = \frac{1}{2}$ and $g = 2$, so that $mg = 1$, and it is for this reason that the Bohr magneton was observed in the original Stern-Gerlach experiment with silver vapour. Since, for the elements zinc, cadmium and mercury, for example, the fundamental term is 1S (simple) with $j = 0$, and hence $m = 0$, it follows that the magnetic moment is zero.

For thallium, spectroscopy shows that the fundamental term is the doublet term p_1 , for which $l = 1$, $j = \pm \frac{1}{2}$, $m = \pm \frac{1}{2}$. To this corresponds the splitting factor $g = \frac{2}{3}$, and thus $mg = \frac{1}{3}$. This explains the experimental result obtained by Gerlach.

The deviation s of an atomic ray under the action of the magnetic field is readily obtained. If t is the time during which the force producing an acceleration g is in action, $s = \frac{1}{2}gt^2$. Putting v for the velocity of the atom and l for the length of path in the magnetic field, clearly $t = \frac{l}{v}$. If $\frac{dH}{dz}$ is the *gradient* of the field, the acceleration g is given by :

$$g = \frac{dH}{dz} \times \frac{\text{magnetic moment of the atom}}{\text{mass of the atom}}.$$

The mean velocity of the atoms in the beam is furnished by

* The *fundamental term* of a series corresponds to the lowest energy level. For the elements of the first and second groups, it is an s term ; for aluminium, indium, and thallium a p term.

kinetic theory, $Mv^2 = 3RT$, so that we obtain finally for the displacement s of the atomic rays on the photographic plate :

$$s = \frac{1}{2} \frac{\mu}{M} \left(\frac{l}{v^2} \right) \frac{dH}{dz} = \frac{\mu}{6R} \frac{l^2}{T} \frac{dH}{dz},$$

where μ is the magnetic moment of the atom and R is the gas constant. The temperature T and the field gradient $\frac{dH}{dz}$ are known experimental data. The field H (and its gradient) is determined by measuring the repulsive force on a fragment of bismuth wire placed in the field.

In the case of silver, if the atomic magnetic moment μ is to equal 1, the observed deviation should be given by :

$$s = 1.12 \times 10^{-5} \frac{l^2}{T} \frac{dH}{dz} \text{ (cm.)}$$

or for $l = 3.3 \text{ cm.}, T = 1,000^\circ, \frac{dH}{dz} = 10^4 \frac{\text{gauss}}{\text{cm.}},$

$$s = 1.12 \times 10^{-3} \text{ cm.}$$

This is precisely the value found by Gerlach and Stern. Expressed in another way, Gerlach and Stern's measurements of the deviation lead to a value for the magnetic moment of silver equal to 5,400 to 5,700 $\frac{\text{gauss} \times \text{cm.}}{\text{mol.}}$, whilst the theoretical value is, as we know, 5,560.

These celebrated experiments must be counted among the most important of contemporary physics. Not only do they provide a means for confirming experimentally the theoretical value of the magneton but, at the same time, they constitute a direct proof of the *spatial quantisation* of the magnetic moment of an atom in a magnetic field, as predicted and required by the quantum theory.

Similar measurements were later performed by Taylor for hydrogen, sodium, and potassium, the deviation in each case corresponding to an atomic moment of *one magneton*. Other important investigations are due to Leu of Hamburg (1927).*

* Leu, *Zeits. f. Physik*, 41, p. 551, 1927.

The Magneto-mechanical Effect (Einstein and de Haas)

Richardson pointed out in 1908 that the magnetisation or demagnetisation of a body should produce a mechanical effect due to the inertia of the atoms. That this should be so is clear when we realise that the relation $\text{magnetic moment} = \frac{e}{2m_0}$ (moment of momentum) or $M = \frac{e}{2m_0} J$,* which holds good for a single electron, must also be true for a body of macroscopic dimensions. This follows from the fact that the M and J corresponding to any electron are parallel vectors, and forming the vector sum over all the electrons, the resultant M and resultant J will obey the same relation as each pair of components.

In 1915 Einstein and de Haas† succeeded in devising an experimental arrangement which enabled the effect in question to be measured and the value of the ratio M/J determined. The experiment consisted in subjecting a suspended magnetic needle to an alternating magnetic field, the period of which was adjusted to equal the period of free oscillation of the needle. The experiment was later repeated by various workers. The surprising but well-established result of these researches on iron, nickel, cobalt, etc., is that the ratio M/J does not equal $\frac{e}{2m_0}$ as required by the electron theory, but has, instead, exactly double this value.

In the experiments of Einstein and de Haas a small iron or nickel bar was suspended by a wire so that it could rotate about its longitudinal axis. A powerful magnetic field was arranged to

* This relation is also written $\frac{M}{J} = \frac{e}{2m_0c}$ where e is expressed in electrostatic units.

For a single electron describing a circular orbit with a frequency of n revolutions per second, the equivalent current $i = \frac{ne}{c}$, and the corresponding magnetic moment $M = \pi r^2 \frac{ne}{c}$. The moment of momentum $J = m_0 2\pi r n \cdot r$, so that we obtain directly,

$$\frac{M}{J} = \frac{e}{2m_0c}.$$

† And later E. Beck, *Ann. d. Physik*, 60, p. 109, 1929

magnetise the rod. On reversing the field direction instantaneously by reversing the current in the magnetising solenoid, the rod was subjected to an impulsive force resulting in a perceptible rotation. To magnify the effect and to eliminate disturbing factors, the experimenters had the excellent idea of using an alternating magnetic field of the same periodicity as the free oscillations of the pendulum system formed by the suspended bar. When this was done the bar executed forced oscillations of frequency equal to that of the current in the magnetising solenoid. With sinusoidal variation of the current, the oscillations of the bar are sinusoidal and, despite the frictional resistance to motion, are maintained, *i.e.*, the amplitude does not fall off with time.

From the amplitude of the oscillations the moment of momentum (per unit volume) J was deduced. The magnetic moment (also per unit volume) M was known from the intensity of the current in the solenoid. The results should have agreed with the equation :

$$\frac{J}{M} = \frac{2m_0}{e} = 1.13 \times 10^{-7}.$$

Actually, however, the value found for $\frac{J}{M}$ was exactly half the theoretical result, namely, 0.57×10^{-7} .

It may be noted that, to avoid the direct determination of the damping coefficient of the system, the following method was adopted : Instead of measuring the angular deflection appropriate to perfect resonance, several amplitudes were determined for frequencies of the exciting current differing slightly from the characteristic frequency of the oscillating system. By the theory of oscillations the damping coefficient could then be determined by a method which for the sake of brevity we shall not go into here. The appearance of the ratio $\frac{e}{m_0}$, the specific charge of the

electron, in the results of these famous experiments of Einstein and Haas, provides direct evidence of the part played by the electron in magnetic phenomena.

The inverse effect to the one just described, was discovered and

measured by S. J. and J. S. Barnett * in 1915 and 1917. They rotated a cylindrical iron rod about its axis and measured the magnetic moment acquired as a result of the rotation.

Let us examine the conclusions to which these important experiments lead. If the moment of the elementary magnets is due to the orbital motion of electrons, the mechanical moment

associated with unit magnetic moment will equal $\frac{2m}{e}$. If, on the

other hand, the intrinsic magnetic moment of the electrons is responsible for the elementary magnetic moment, then the corresponding mechanical moment has half the above value, and this should be observed when the *electrons* are orientated with their axes in the same direction. The hypothesis of the rotating electron explains perfectly the anomaly which the gyromagnetic effect had brought to light, for the rotating electrons will orientate themselves with their axes parallel to the direction of magnetisation and will impart their mechanical moments to the body of which they form part, giving the latter an angular velocity.

Thus we may say that all magnetic phenomena depend on the existence of elementary magnets, and have their origin in the motion of electrons or in the intrinsic magnetisation of the latter.

Phipps and Taylor's Experimental Determination of the Magnetic Moment of the Hydrogen Atom (1926) †

The magnetic moment of the hydrogen atom is of particular interest because the hydrogen atom lies at the base of the calculation of the unit of magnetic moment, and possesses a moment of one Bohr magneton.

The difficult experimental determination of the magnetic moment of the hydrogen atom was made in the physical chemistry laboratory of the University of Illinois, by Professors T. E. Phipps and J. B. Taylor ‡ using the method of Gerlach and Stern.

The hydrogen was produced by means of a Wood tube (to be described later) and the pencil of atoms, delimited by suitable apertures, impinged on a plate coated with molybdenum trioxide. The latter when chemically reduced gave a blue line on a white ground, indicating the point of impact of the rays.

The atomic pencil passed through a powerful non-uniform magnetic field which split it into two branches. There was also an undeviated line attributable to active hydrogen. By measuring the deflection of the rays,

* S. J. Barnett, *Phys. Rev.*, 6, p. 239, 1915.

† Wrede has also measured the magnetic moment of hydrogen and found the value, one magneton. See *Zeits. f. Physik*, 1927.

‡ Phipps and Taylor, *Phys. Rev.*, 29, p. 319, 1927.

the magnetic moment was calculated and found to equal within the limits of experimental error—which are rather high—exactly one Bohr magneton.

A number of further details may be mentioned. As already stated, Stern and Gerlach worked with copper and gold as well as silver vapour. Taylor tried sodium and potassium and found the atoms of these elements to have a moment of one Bohr magneton.

The formula employed by Phipps and Taylor in working out their results was not as a matter of fact the simple expression given above, but a modified form embodying a pair of corrections. One of these takes account of the fact that the exit velocity of the atoms from the aperture in the furnace is not determined accurately by the equation $\frac{1}{2} MC^2 = RT$ owing to the disturbing effect of collisions. These result in C having a *larger* value more nearly equal

to $\sqrt{\frac{3.5 RT}{M}}$. The second effect for which correction must be made is that, as a particular atom is deviated in its passage between the pole pieces, it occupies at successive instants points at which the field gradient $\frac{dH}{dz}$ is not the same, because this gradient varies in passing transversely from the knife edge to the hollowed out pole piece. The correction necessary will depend obviously on the length of path l , the velocity of the atom and its magnetic moment. The following is the corrected formula adopted by Phipps and Taylor.

$$\frac{1}{\text{Moment}} = \frac{1}{2s} \left(\frac{dH}{dz} \right)_0 \frac{l^2}{3.5 RT} \left\{ 1 + \frac{l^2 \text{ Moment}}{12 \times 3.5 RT \cdot s} \left(\text{var. of } \frac{dH}{dz} \right) \right\}.$$

Here s is the deviation, $\left(\frac{dH}{dz} \right)_0$ is the value of the field gradient at the point of entry, and l is the length of the poles. The coefficient 3.5 was obtained by Stern in his direct measurements of atom velocities.

Without entering into a long description of Phipps and Taylor's apparatus, we may point out that it was essential to have a very fine pencil of rays. Three delimiting apertures were used each of length 3 mm. and not more than 0.075 mm. wide. These were made by constricting a glass tube at three places on to a stretched steel ribbon of the desired breadth and thickness. The steel was then dissolved by immersion in an acid bath. The glass had, of course, to be carefully annealed so that no change of form occurred.

This part of the apparatus was attached to the Wood tube containing hydrogen at low pressure (0.12 mm.), across which an electric discharge was passed. In the space between the first and second apertures a pump operated, and another pump was connected between the second and third apertures, with which the pressure was reduced to 0.0001 mm.

In this way the free paths of the atoms were increased so that they were effectively free atoms. The detecting plate was a glass surface coated, as already stated, with molybdenum trioxide by exposing the plate to the smoke of molybdenum burning in an oxygen flame. On reduction the trioxide turns a dark blue clearly visible on white. For determining the exact positions of the deviated lines microphotographs were taken, using a known scale of graduations to give directly the distance s with precision.

The dissociation of the hydrogen into atoms is not complete, and it is the undissociated chemically active molecules which give rise to the central line.



FIG. 64.

known about the solid state and about the constitution of dissolved substances, contradicts the supposed freedom of orientation.

As regards the second of Langevin's fundamental hypotheses, the applicability of classical statistical mechanics, it should be noted that in 1905, when Langevin propounded his theory, the doctrine of quanta, according to which in presence of a magnetic field the magnetic moment can assume only a few fixed discrete positions, had not yet been developed. At the present time, after the experiments of Gerlach and Stern, and also thanks to spectroscopic research, there can no longer be any doubt that the magnetic moment of atoms *free to rotate* must be subject to the effect of quantisation in the way foreseen by Sommerfeld.

In any case it is impossible to speak of orientation for the atoms in solid bodies and—perhaps—also for dissolved molecules.

Also, as we shall show immediately, in the case of diatomic gases such as oxygen and nitric oxide (NO), the experimental values cannot be obtained as multiples of the theoretical magneton. Pauli attempted the first explanation on the basis of quantum theory, of these facts, in 1920.

Precise measurements by Weiss and Piccard on oxygen O_2 and nitric oxide (NO) have furnished for the magnetic moments of these gases the values :

1.8 Bohr magnetons for nitric oxide,

2.8 ,, ,, ,, oxygen,

deduced from the relation :

$$\text{Moment of the gramme atom } M = \sqrt{3RC}.$$

C is the Curie constant for a gramme molecule.

Turning back for a moment to the reasoning on which the above formula is based (p. 235) we observe that in taking the sum of the projections of the elementary moments on the direction of the field, it was supposed that these moments might assume all possible orientations. If this assumption is not made, it is easy to show that the following relation would be arrived at :

$$C = \frac{M^2}{R} \overline{\cos^2 \theta},$$

in which R is again the gas constant, M the magnetic moment of

a gramme molecule, $\overline{\cos^2 \theta}$ the mean square of the cosine of the angle between the axis of the elementary moment and the field direction, for all permissible orientations.

Langevin theory, which appeared before the quantum theory, regarded θ as being continuously variable and substituted therefore for $\overline{\cos^2 \theta}$ the value appropriate to this case, namely, $\frac{1}{3}$.

The quantum theory, however, asserts that the orbits, and hence the resulting magnetic moments, can assume only a few discrete positions with respect to the direction of the external field, these positions depending upon the quantum number with respect to that direction.

Stated more precisely, if the quantum number n is 1, one direction only is possible for the elementary magnets, which all arrange themselves parallel to the field. For this condition the mean cosine squared is 1 and not $\frac{1}{3}$, so that the correct formula to substitute for Langevin's becomes :

$$C = \frac{M^2}{R}.$$

If $n = 2$ there are two possible positions and the planes of the orbits may be disposed either perpendicular to the lines of force or inclined to them at an angle of 30° . Thus $\cos \theta = 1$ or $\cos \theta = \frac{1}{2}$, and the average value of $\cos^2 \theta$ is now :

$$\frac{1}{2} \left(1 + \frac{1}{4} \right) = \frac{5}{8}.$$

For $n = 3$ there are three cases :

$$\cos \theta = 1 \qquad \cos \theta = \frac{1}{2} \qquad \cos \theta = \frac{2}{3}.$$

It can be shown generally that for a given quantum number n there exist n equally probable positions of the elementary axes, and the mean square of their inclinations with respect to the field is given by the relation :

$$\overline{\cos^2 \theta} = \frac{1}{3} \frac{(n+1)(2n+1)}{2n^2}, *$$

which, when n is very large, reduces to : $\overline{\cos^2 \theta} = \frac{1}{3}$.

* This formula follows from the fact that the sum of the squares of the integers from 1 to n has the value :

$$\sum_1^n x^2 = \frac{n}{3} (n+1) \left(n + \frac{1}{2} \right).$$

The point discussed here is obviously sufficient to obscure the direct interpretation of the experimental results which will no longer come out to be multiples of the theoretical magneton if the moments per gramme molecule are deduced from the expression :

$$C = \frac{1}{3} \frac{M^2}{R}.$$

In addition to the above, there is also the difficulty in obtaining accurate experimental data.

Pauli has interpreted the value 1.8 obtained for the magnetic moment of nitric oxide, using the formula :

$$C = \frac{M^2}{R} \quad \text{or} \quad M = \sqrt{RC},$$

which we have just seen corresponds to the assumption of $n = 1$. Langevin's formula furnishes a value $\sqrt{3}$ times greater, and the experimental result has therefore to be divided by $\sqrt{3}$. One obtains $\frac{1.80}{1.73}$, that is, approximately one Bohr magneton.

Similarly, if n equals 2, the correct expression to apply is :

$$C = \frac{M^2}{R} \frac{1}{\cos^2 \theta} = \frac{M^2}{R} \frac{5}{8},$$

that is,

$$M = \sqrt{\frac{8 RC}{5}}$$

in place of the Langevin result, $M = \sqrt{3CR}$.

The ratio of the latter value to the preceding one is $\sqrt{\frac{15}{8}} = 1.37$, so that instead of two magnetons it is clear that 2.74 will be obtained, and, in fact, oxygen gives the result 2.8. In the molecule of oxygen therefore the two atoms must be joined in such a way that their individual moments add up.

It should be noted that the extension of the quantum rule established for the hydrogen atom, to polyatomic molecules, is purely speculative, as molecular models of diatomic gases are as yet unknown to us. Unfortunately, also there, exist no monatomic

paramagnetic gases. The only paramagnetic gases which have been properly studied are oxygen and nitric oxide.

This theory of Pauli's has been modified by other authors to take into account the magnetic behaviour of the atom, as shown by the so-called anomalous Zeeman effect.

Pauli supposes that the elementary magnets behave in the same way as the atom of hydrogen, that is, with splitting factor g equal to one. We know however that in general g is not *unity* and that the magnetic moment resolved in the direction of the field equals $mg\mu_0$, where m assumes the value $j, (j-1), (j-2), \dots -j$ and g has corresponding values. μ_0 represents the Bohr magneton.

Thus in place of μ , which occurs in Langevin's calculation, for a *monatomic gas*, we must substitute in the fundamental formula of Langevin $\left(C = \frac{\mu^2 N^2}{3R}\right)$ the *apparent moment* of the atom with the value,

$$\mu' = g\mu\sqrt{j(j+1)}.$$

This follows from the demonstration which is given in the footnote on page 263. Finally we obtain,

$$C = \frac{N^2 \mu_0^2}{3R} g^2 j(j+1). \quad \dots \quad (\alpha)$$

The apparent moment $\mu' = g\mu_0 \sqrt{j(j+1)}$ tends to the value $g\mu_0 j$ when j is very large.

It is now clear why, knowing only the experimental value of the Curie constant, it was not possible to obtain the value of the magnetic moment μ but only the quantity $g \sqrt{j(j+1)}$. Actually, if in (α) , in place of μ_0 , $\frac{eh}{4\pi m_0 c}$ is substituted, and if the numerical values of c , e , h and m_0 are inserted, we obtain,

$$g \sqrt{j(j+1)} = 2.83 \sqrt{C} \quad \dots \quad (\beta)$$

Only the elements iron, palladium, the platinum metals and the metals of the rare earths have paramagnetic ions in solution. The verification of the formula $\mu' = g\mu_0 \sqrt{j(j+1)}$ will be possible only if the values of g and j are known, and hence it will be

necessary to determine g and j from measurements of the Zeeman effect of the corresponding *spark spectra*.

Doctor Hund, of the University of Göttingen, in an experimental study of the ions of the metals of the rare earths, was able to establish the correctness of equation (β) as the values of g and j are furnished by spectroscopy and the constant C was known from measurements of Cabrera and St. Meyer.*

The Magnetic Susceptibility of Alkali Vapours

Until Gerlach and Stern's famous experiments, establishing the directional quantisation of the magnetic axis, the point of departure for the calculation of the paramagnetic susceptibilities of gases and solutions was Langevin's law, which assumed a magnetic moment rigidly attached to the atom itself.

Developing the theory of the orientating effect of the field on the atoms, superimposed on their thermal agitation, the equation already established, $C = \frac{\mu^2}{3k}$ with $k = \frac{R}{N}$ is obtained. μ is the magnetic moment of the atom, C Curie's constant and R the gas constant. From this equation it follows at once that if the atom of the gas concerned has a magnetic moment of one *magneton*, the Curie constant should have the value $C = 0.12$. We have, in fact, if $\mu = 0.92 \times 10^{-20}$,

$$C = \frac{0.81 \times 10^{-40}}{3 \frac{R}{N}} = \frac{0.81 \times 10^{-40} \times 60.6 \times 10^{22}}{3 \times 13.7 \times 10^{-17}} = 0.12.$$

In this calculation of Langevin's it is assumed—we repeat—that the atoms can turn so that their magnetic axes are inclined in any direction in the field, and it is also assumed that the Maxwell-Boltzmann statistics determine the relative probabilities of different orientations.

The experiments of Gerlach, Stern and Taylor lead to an entirely different result and show that the magnetic moment is

* F. Hund, "Linienpektren und periodisches System des Elemente," 1927. B. Cabrera, *Comptes Rendus*, 180, 1925. St. Meyer, *Phys. Zeits.*, 26, 1925. For further details, see E. Bloch, "L'ancienne et la nouvelle théorie des quanta," 1930.

orientated parallel or antiparallel to the field direction. For silver, potassium, sodium, etc. (monovalent atoms), the experiments have provided a direct measurement of the magnetic moment which is found to equal one magneton (0.92×10^{-20} c.g.s. units).

When directional quantisation must be assumed, as in the case of dense gases, it is necessary to modify Langevin's theory and the theoretical expression becomes as already shown, $C = \frac{\mu^2}{k}$, giving a Curie constant three times the value 0.12.

A. Roth, of the Physical Institute of Tübingen, using a method which we shall not describe, measured the susceptibility of alkali vapours and found, as the mean of many determinations, $C = 0.38$ (probable error $\pm 10\%$). That is to say, he actually found the triple value for the Curie constant, anticipated by theory.*

Thus we arrive at the result that the alkali vapour at a pressure of some millimetres, is completely *quantised* in the orientation of the magnetic moments. The experiment confirms the interchange of magnetic energy μH and thermal energy kT and disproves the continuous distribution of the magnetic axes which rests on the kinetic interpretation of temperature equilibrium.

Now, the number of collisions experienced by an atom per second is easily obtained from the kinetic theory, given the conditions of the gas. It is found that a *quantised* orientation remains undisturbed, only for a period of the order, 10^{-11} seconds. This shows that a *mechanical* interpretation of spatial quantisation is without meaning, for if the direction of the magnetic moment were modified by the collision, an atom would change its orientation every 10^{-11} seconds and that would involve a thermal emission of light of much greater amount than actually occurs.

Ehrenfest has suggested that the magnetic axis may not be so intimately connected with the atom as to participate in the latter's mechanical or thermal motion.

* See Report of W. Gerlach to the Como Congress, 1927. These measurements of Roth on potassium were made in a range of pressure variation from 0.5 to 30 mm. of mercury, and at temperatures from 600° to 800° absolute.

To-day, however, it appears more natural to abandon altogether any *mechanical* conception of directional quantisation and its modification by collisions.

In connection with this point, we must bear in mind measurements of dispersion, which show conclusively that a magnetised gas exhibits no trace of optical anisotropy, so that the quantisation with respect to the field direction cannot consist of an orientation in space of the orbits of the dispersion electrons. Experiments by Schulz on sodium vapour in a magnetic field failed to detect any double refraction, although we know, from Taylor's researches, that the magnetic moments behave as if they were all orientated.

It is of interest to note that the new quantum mechanics overcomes, at least formally, this difficulty associated with the Langevin expression. For, consider the formula :

$$\text{susceptibility per gramme molecule} = \frac{\mu^2 N}{3kT} \quad . \quad . \quad . \quad (*)$$

The moment is shown to be given by :

$$\mu^2 = g^2 \mu_0^2 j(j+1), *$$

where g = Landé's splitting factor,

μ_0 = the Bohr magneton,

j = the impulse moment.

For the atoms of the alkalis in their normal state, Landé's

* Proof of the formula $\mu^2 = g^2 \mu_0^2 j(j+1)$.

The magnetic energy of an atom in a field H , in the quantum state m , is

$$E_m = -mg\mu_0 H \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

for it is known from the Zeeman effect that the magnetic moment resolved in the direction of the field equals $mg\mu_0$. (1) corresponds to the Langevin expression

$$E_m = -\mu H \cos \theta.$$

The Boltzmann statistical law has now to be replaced by one corresponding to the discontinuous series of values of E_m . The probability W_m of a quantum state of magnetic energy E_m is given by,

$$W_m = B e^{-E_m/kT} = B e^{mg \frac{\mu_0 H}{kT}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The constant B is determined by the single condition that the total probability W for m varying through integral values from $-j$ to $+j$ must

factor g has the value 2, and $j = \frac{1}{2}$, so that $j(j+1) = \frac{3}{4}$. Putting these values in (*), the latter becomes,

$$\text{susceptibility} = 4\mu_0^2 \frac{3}{4} \frac{N}{3kT} = \frac{\mu_0^2 N}{kT},$$

from which the factor $\frac{1}{3}$ has disappeared.

In this theory, the question of the disturbance of the direction of quantisation in collisions due to thermal agitation, has no longer any meaning.

be unity. If $\frac{\mu_0 H}{kT}$ is small—weak quantisation—so that its square can be neglected, we have :

$$e^{mg \frac{\mu_0 H}{kT}} = 1 + mg \frac{\mu_0 H}{kT},$$

and it is easy to show that $B = \frac{1}{2j+1}$ (observing that $\sum_{m=-j}^{+j} m = 0$, and that there are altogether $2j+1$ possible states). We obtain therefore

$$W_m = \frac{1}{2j+1} \left(1 + \frac{mg\mu_0 H}{kT} \right).$$

The *mean value of the magnetic moment* is clearly given by the sum of the possible moments multiplied by their respective probabilities, *i.e.*, by

$$\sum_{m=-j}^{m=+j} W_m \times mg\mu_0.$$

Thus

$$\text{mean magnetic moment } \bar{\mu} = \sum_{m=-j}^{m=+j} W_m mg\mu_0 = \frac{g\mu_0 H}{kT} \frac{1}{2j+1} \sum m^2,$$

$$\text{and since } 1^2 + 2^2 + \dots + j^2 = \frac{j(j+1)(2j+1)}{2 \cdot 3}$$

we have finally :

$$\text{mean magnetic moment } \bar{\mu} = \frac{g^2 \mu_0^2 H}{3kT} j(j+1),$$

and, for the susceptibility $\mu \times \frac{\text{Avogadro's Number}}{H}$,

it follows that,

$$\text{susceptibility} = \frac{1}{3} \frac{g^2 \mu_0^2 N}{kT} j(j+1).$$

To sum up, we may say that the result of the calculation of susceptibility according to quantum mechanics gives a similar expression to Langevin's

$$\left(\frac{1}{3} \frac{\mu^2 N}{kT} \right)$$

but in place of the true magnetic moment of the atom of the substance concerned, appears an *apparent magnetic moment* given by

$$\mu' = g\mu_0 \sqrt{j(j+1)}.$$

Quantum mechanics leads thus to the following result :

$$\text{susceptibility} \times T = C_0 g^2 j(j+1) = C_j \quad . \quad . \quad . \quad (*)$$

In this relation C_0 is the Curie-Langevin constant, g Lande's factor, and j the internal quantum number of the atom in its fundamental state.

It must be pointed out that the relation (*) is strictly valid only if the fundamental level of the atom is *simple*, for if it be multiple, when the atom is thermally excited, the product *susceptibility* \times *temperature* instead of remaining constant, assumes the mean value of the Curie constants corresponding to the normal sublevel and the excited levels. The expression (*) is again true if kT (energy) has a value small in comparison with $h\Delta\nu$, $\Delta\nu$ being any of the frequencies corresponding to transitions between the excited levels and the highest state of the multiple level. Researches on this subject are due to Professor Rita Brunetti (University of Cagliari), to whose original papers * reference should be made.

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* *Rendic. Acc. Lincei*, 1929 ; *Nuovo Cimento*, N. 3, 1929.

CHAPTER VIII

WAVE MECHANICS AND QUANTUM MECHANICS APPLICATIONS

THE history of theoretical physics in the twentieth century may be divided broadly into two periods. In the former of these, extending from Planck's fundamental discovery of the radiation formula in 1900, to the year 1924, the men in the forefront were Planck, Einstein, Bohr and Sommerfeld. The second period covers the time from 1924 to the present day, and the outstanding figures are L. de Broglie, Schrödinger, Born, Jordan, Fermi and Dirac.

It may be said that Einstein was the prime mover in the formulation of the corpuscular theory of radiation which, after leading to an acceptable interpretation of the photoelectric effect, successfully explained the Compton effect, and assumed an equal place by the side of the wave theory. The older wave theory could not be abandoned however, and in practice physicists were led to adopt a kind of dualistic principle, treating light as waves in the discussion of one class of experiments, and as particles in the discussion of others.

During the development of the corpuscular theory of radiation Bohr had put forward his fundamental law $\nu = \frac{\Delta W}{h}$ and had arrived at a remarkable interpretation of line and band spectra, as well as of the experiments of Franck, Hertz and K. T. Compton, on collisions.

There were, however, many gaps and obscurities. With de Broglie and Schrödinger commences the second period of contemporary physics, which has witnessed the simultaneous development of wave mechanics, and matrix mechanics, now practically fused into one theory, known as *quantum mechanics*.

Introduction

Despite the remarkable achievements of Bohr's theory there still remained in some minds an uneasy sense of something unsatisfactory. The selection of the stationary orbits of hydrogen which lies at the base of the whole theory was arrived at by a method which savoured of artifice, namely, by the postulation of the equations $\int p_\phi d\phi = nh$, $\int p_r dr = nh$, determining from among all possible orbits of the electron the "permissible" orbits, corresponding to stationary states of the atom.

It was certainly true that this method gave a complete explanation of all the properties of the hydrogen spectrum, its fine structure, and the effect of perturbations (Stark and Zeeman effects), but still the method had not been justified. Moreover, how was it possible for the electron, in its circular motion about the nucleus, not to radiate energy? This was contradictory to Maxwell's electromagnetic theory, verified by innumerable experiments in all kinds of ways, in its most remote consequences. The Bohr-Sommerfeld theory was not a logically perfect system or well-defined structure. It left unexplained the contradiction with the classical laws of electromagnetism, and it introduced the hypothesis of discontinuity without justification, postulating simply that certain magnitudes could assume only values which were integral multiples of a universal constant (*e.g.*, the moment of momentum had to be a multiple of h). The quantum theory had limited itself to affirming in a particular way, that nature abhors fractional numbers—a truly Aristotelian proposition.

Nor was this the only imperfection in the theory, for, as we have seen in the "anomalous" Zeeman effect, the quantum rule is subject to an exception and the numbers $\frac{1}{2}$, $\frac{3}{2}$, $\frac{5}{2}$. . . , must be allowed in addition to the integers.

In defence of the quantum doctrine, it must be remembered that the theory was not constructed by a rigorously deductive method, but grew out of successive hypothesis enabling the immediate experimental facts to be explained. It is natural to suppose that much more general assumptions would be equally successful in accomplishing this end.

The inadequacies of the Bohr theory, especially in connection with the problem of the helium atom, again drew the attention of physicists to its inherent difficulties which had been forgotten in the brilliant successes of the earlier years.

A way out of the crisis to which matters had arrived in 1923, could only be hoped for in a new generalisation of mechanics—as we may well call it—which would embrace in a new form not only Galileo's but also Einstein's system.

Einstein's mechanics were designed to apply in the domain of enormous velocities, whilst for the ordinary velocities the mechanics of Galileo and Newton remained valid. Similarly, the new doctrine would have to give, in its applications to atomic problems, results in agreement with experiment, whilst in its applications to macroscopic problems its results would necessarily coincide with those furnished by classical mechanics.

It was also to be desired that the mysterious quantum conditions, indispensable for the interpretation of atomic phenomena, should arise naturally and should no longer be extraneous additions, unconnected with the rest of the theory. Finally one hoped that in the new system, the difficulties which had successfully obstructed the Bohr-Sommerfeld methods would be overcome. These methods had, in fact, shown themselves powerless to deal with the problem of the hydrogen molecule and the problem of the helium atom, and had in some cases given results in contradiction with experiment.

The new line of advance was found in the years 1925–26 through the coherent, logical reorganisation of atomic physics. The credit of this work is due to a number of scientists. Heisenberg, Born, Jordan and Dirac developed *quantum mechanics*, of which we can only speak briefly, and, independently, de Broglie and Schrödinger created "*wave mechanics*." These two doctrines are in reality diverse forms of theory which lead to the same results. We ought, in view of its importance, to discuss fully Heisenberg's mechanics as well as, or even in preference to, wave mechanics, but this we shall not do, principally because it would take too long and also because the argument is unlikely to be understood other than by specialists.

Heisenberg, Born, Jordan and Dirac, giving up the attempt to provide any geometric or mechanical model of the atom, have

found a way of connecting together the various magnitudes characterising the radiations emitted by an atom—wave-length, intensity, polarisation, etc.—without introducing quantities not observable experimentally, that is, making no use of quantities such as, for example, the variables determining the motion of the electron in the atom (period of revolution, velocity, phase).

The other attempt to incorporate the Bohr postulates into the coherent system of a general theory was made by Professor Schrödinger, of the University of Zürich (now of the University of Berlin). Schrödinger developed and rendered more precise certain ideas of Louis de Broglie,* and proposed a theory which has received the name of *wave mechanics*.

So as not to interrupt the main course of the argument by long parentheses, it will be useful to insert here a brief account of the theory of vibrating systems, which is a necessary preliminary to a proper understanding of wave mechanics.

Resumé of Acoustical Theory. Examples of Vibrating Systems

Consider an infinitely long stretched string placed along the x axis. Suppose the tension in the string to be T and its mass per unit length ρ . It is easy

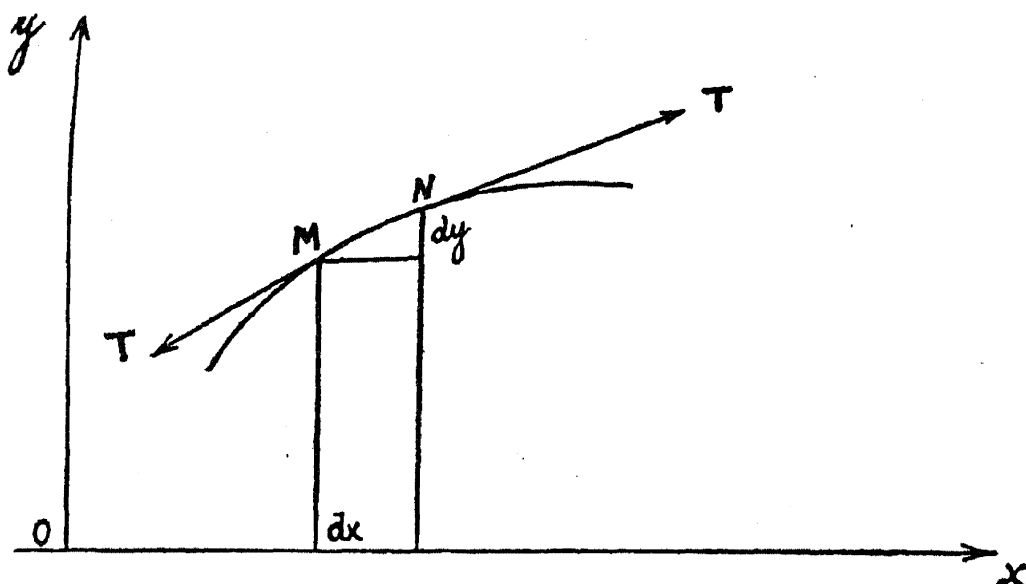


FIG. 65.

to obtain the differential equation relating the displacement y of any point of the string, with its abscissa x and the time t (see Fig. 65).

* Louis de Broglie is the brother of Maurice de Broglie to whom we owe important researches on X-rays.

We have here the characteristic problem of the vibrating string considered by Pythagoras five centuries before Christ.

It is easily verified that y so defined as a function of the two variables x and t satisfies equation (3) whatever the values of the parameters A , B , C and D . But $f(x)$ must be zero at the extremities of the string, which are fixed, so that we have $A = 0$ and $\sin mL = 0$. The latter condition implies that the constant m can assume only the following values :

$$m = \frac{K\pi}{L}, \quad \dots \quad (5)$$

where $K = 1, 2, 3, 4 \dots$

Thus the string fixed at its ends can vibrate only in a discrete series of modes, the possible wave-lengths and consequently the frequencies of the vibrations permitted are strictly determined (see Fig. 66).

The fact that m can assume only a discontinuous series of values corresponds in the acoustical problem to the well-known fact that a violin string vibrates in a number of modes. In the K^{th} mode there are $K - 1$ intermediate nodes (stationary positions). The possible frequencies are

$$\frac{u}{2L}, \frac{2u}{2L}, \frac{3u}{2L} \dots$$

Case of Stretched Membrane

The problem of a stretched membrane involves one more variable than is required in the case of the stretched string. The displacement z of a point in the membrane, from the equilibrium plane, is a function of the two positional co-ordinates x , y , and of the time t . A practical example of a stretched membrane is provided by a telephone earpiece.

The differential equation for the motion of the membrane is obtained in a similar way to that given above for the stretched string and takes the form :

$$\Delta_2 z = \frac{\partial^2 z}{\partial x^2} + \frac{\partial^2 z}{\partial y^2} = \frac{1}{u^2} \frac{\partial^2 z}{\partial t^2} \quad \dots \quad (6) *$$

u being the velocity of propagation of a sinusoidal wave in any direction, on a membrane of infinite dimensions.

We consider now the behaviour of a circular membrane clamped along its boundary. It is evident that polar co-ordinates are more suitable than cartesian for dealing with this case. The connection between the polar co-ordinates r , θ and the cartesian co-ordinates x , y is contained in the equations :

$$\begin{aligned} x &= r \cos \theta \\ y &= r \sin \theta \end{aligned}$$

and making use of these results the differential equation (6) is transformed into the equivalent form :

$$\Delta_2 z = \frac{\partial^2 z}{\partial r^2} + \frac{1}{r} \frac{\partial z}{\partial r} + \frac{1}{r^2} \frac{\partial^2 z}{\partial \theta^2} = \frac{1}{u^2} \frac{\partial^2 z}{\partial t^2} \quad \dots \quad (7)$$

We now try to find a solution of the above equation by putting z equal to the product of three functions, $f(r)$. $F(\theta)$. $g(t)$, f a function of r only, F a

* The "Laplacian operator," $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}$, is denoted for brevity by the symbol Δ_2 .

function of θ only, and g a function of t only. Substituting in (7) and dividing by z we obtain :

$$\frac{1}{f} \frac{\partial^2 f}{\partial r^2} + \frac{1}{rf} \frac{\partial f}{\partial r} + \frac{1}{r^2 F} \frac{\partial^2 F}{\partial \theta^2} = \frac{1}{u^2 g} \frac{\partial^2 g}{\partial t^2} = -m^2 \quad \dots \quad (8)$$

The left-hand side of the equation is independent of t , the right-hand side is dependent of r and θ . Both sides of the equation must therefore equal a constant, independent of r , θ and t , which we shall denote by the symbol $-m^2$.

Thus, it follows that $\frac{1}{u^2 g} \frac{\partial^2 g}{\partial t^2} = -m^2$, and this is identical with the differential equation of the stretched string. The solution can be written down at once :

$$g(t) = A \cos mut + B \sin mut.$$

Returning now to the left-hand side of (8), this leads to the equation :

$$\frac{r^2}{f} \frac{\partial^2 f}{\partial r^2} + \frac{r}{f} \frac{\partial f}{\partial r} + m^2 r^2 = -\frac{1}{F} \frac{\partial^2 F}{\partial \theta^2} = l^2 \quad \dots \quad (9)$$

Here l^2 is a constant, and its introduction in this way is justified by an argument exactly similar to that just given with respect to m^2 . It follows at once that,

$$F(\theta) = C \cos l\theta + D \sin l\theta \quad \dots \quad (10)$$

Remembering that θ is a cyclical co-ordinate, like longitude on the earth, it is clear that when θ increases by 2π , $F(\theta)$ must return to its original value. For this to be so, l must be integral. Thus

$$l = 0, 1, 2, 3, 4 \dots$$

These obligatory values of l are termed characteristic values or *eigenvalues*.

Finally, as the last stage in the problem, we have the determination of the function $f(r)$ from the differential equation,

$$\frac{\partial^2 f}{\partial r^2} + \frac{1}{r} \frac{\partial f}{\partial r} + \left(m^2 - \frac{l^2}{r^2}\right) f = 0$$

in which l has one of its eigenvalues.

As f (and hence z) is zero for certain values of the radius vector, there exist nodal circles : the nodal lines are l in number.

The Fluid Sphere

This example is introduced because it presents a close analogy with the model of the hydrogen atom as interpreted in wave mechanics.

The vibrations of a fluid confined in a sphere, consist in condensations of pressure which are propagated from point to point with a well-defined velocity, and which are *stationary*; a given point continues to execute the same periodic motion indefinitely. There exist points at which the waves mutually annul each other leaving the fluid particles undisturbed. These form the *nodal surfaces*.

In the vibrating string there are nodal points, in the circular membrane clamped at its periphery, there are nodal lines (circles and straight lines), and similarly in the vibrating sphere of fluid there exist nodal surfaces comprising concentric spheres, meridional planes, and cones.

The starting point of the theory is the fundamental equation of vibrating systems :

$$\Delta_3 \psi = \frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} = \frac{1}{u^2} \frac{\partial^2 \psi}{\partial t^2}$$

ψ representing the condensation (or rarefaction) of the fluid.

The problem is treated in a manner precisely analogous to that used for the membrane, and again it is necessary to introduce *eigenvalues*. We shall meet with the application of this example in connection with the hydrogen atom.

Vibrating Systems in which the Velocity of Propagation Varies from Point to Point

In all the examples of vibrating systems discussed above, the velocity u was a constant at all points. The general wave equation was written :

$$u^2 \Delta \psi = \frac{\partial^2 \psi}{\partial t^2}$$

and contained the velocity u as a constant.

Problems can arise, however, in which u varies with position. An example of such a problem is provided by a stretched string whose density (or diameter) varies from point to point according to some definite law ; u is then a function of x .

If we have the differential equation :

$$\frac{d^2 y}{dx^2} = (a - bx^2) \frac{d^2 y}{dt^2} \quad \dots \quad (1)$$

where a and b are constants, then by comparing it with

$$\frac{d^2 y}{dx^2} = \frac{1}{u^2} \frac{d^2 y}{dt^2}$$

we may say that (1) represents the vibration of a string in which the velocity of propagation varies from point to point according to the law,

$$u = (a - bx^2)^{-\frac{1}{2}}.$$

Problems of this type can also be solved by known methods. We shall shortly meet with applications of such problems.

Schrödinger's Equation

Having explained briefly the elements of the theory of vibrating systems, we now introduce certain general ideas of *classical* or *Newtonian mechanics*. When a mass m is in motion in space, at each point of which it has potential energy V (function of position), then denoting the kinetic energy of the particle by T , we know that $T + V = \text{a constant}$, and this *constant* is the total energy E .

The momenta p_x, p_y, p_z of the mass point with respect to the cartesian axes x, y, z are $m\dot{x}, m\dot{y}, m\dot{z}$ respectively, where $\dot{x}, \dot{y}, \dot{z}$ represent the three components of the velocity.

Since $T = \frac{1}{2}m(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$, it is easily shown that

$$p_x = \frac{\partial T}{\partial \dot{x}} = m\dot{x}, \quad p_y = \frac{\partial T}{\partial \dot{y}} = m\dot{y}, \quad p_z = \frac{\partial T}{\partial \dot{z}} = m\dot{z}.$$

Introducing the function,

$$L = T - V = 2T - E$$

and forming the integral $W = \int L dt = \int 2T dt - E \cdot t = S - E \cdot t$,* it is clear that W is such that :

$$p_x = \frac{\partial W}{\partial x}, \quad p_y = \frac{\partial W}{\partial y}, \quad p_z = \frac{\partial W}{\partial z},$$

i.e., the partial derivatives of W give the momenta.†

The total energy E is the sum of the kinetic energy $\frac{m}{2}(\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$, and the potential energy $V(x, y, z)$, and writing this equation in terms of W we obtain a relation known in mechanics as the Jacobi equation :

$$\frac{1}{2m} \left[\left(\frac{\partial W}{\partial x} \right)^2 + \left(\frac{\partial W}{\partial y} \right)^2 + \left(\frac{\partial W}{\partial z} \right)^2 \right] + V(x, y, z) = E. \quad (1)$$

Now $\left(\frac{\partial W}{\partial x} \right)^2 + \left(\frac{\partial W}{\partial y} \right)^2 + \left(\frac{\partial W}{\partial z} \right)^2$ represents the square of

the *gradient* of the function W , which is determined by its three components along the co-ordinate axes, the quantities $\frac{\partial W}{\partial x}, \frac{\partial W}{\partial y}, \frac{\partial W}{\partial z}$.

Thus,

$$|\text{grad} \cdot W|^2 = \Delta_1 W = 2m(E - V) \quad \dots \dots \dots (2)$$

or, since $\frac{\partial W}{\partial x} = \frac{\partial S}{\partial x}$, etc.,

$$\Delta_1 S = 2m(E - V) \quad \dots \dots \dots (2')$$

to which must be added the equation

$$\frac{\partial W}{\partial t} = -E \quad \dots \dots \dots (3)$$

* $S = \Sigma \int p_k \dot{q}_k dt = \int 2T dt$, and is known as the *action*.

† In fact,

$W = \int 2T dt - Et = m \int (\dot{x}^2 + \dot{y}^2 + \dot{z}^2) dt - Et = m \int (\dot{x} dx + \dot{y} dy + \dot{z} dz) - Et$,
and hence $\frac{\partial W}{\partial x} = m\dot{x} = p_x$ and analogously for $\frac{\partial W}{\partial y}$ and $\frac{\partial W}{\partial z}$.

deduced from

$$W = \int 2Tdt - E t.*$$

As the first step in the wave mechanics, it is affirmed that the two equations (2) and (3) describe a family of wave fronts moving in space with the velocity $u = \frac{E}{\sqrt{2m(E - V)}}$. Consider a surface

σ_0 on which, at a given instant, the function W has at all points the value W_0 . This surface, by definition, is a wave front. There exists another surface σ , close to σ_0 , such that from each point of σ_0 the distance to the nearest point of σ equals $u dt$. After a time dt the value of W on the surface σ is given by

$$W_0 + dW = W_0 + |\text{grad } W| ds + \frac{\partial W}{\partial t} dt = W_0 + |\text{grad } W| u dt - E dt.$$

Now, if the new surface σ is to be the wave front previously located on σ_0 , W must have the original value W_0 , i.e., the quantity $|\text{grad } W| u dt - E dt$ must vanish, or the velocity u at each point must satisfy :

$$u = \frac{E}{|\text{grad } W|} = \frac{E}{\sqrt{2m(E - V)}} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (4)$$

In other words, if at the time $t = 0$, imaginary bullets were projected from all the points of σ_0 in directions normal to the surface and with velocities $u = \frac{E}{|\text{grad } W|}$, these bullets after a time dt would together form the wave front. As the quantity u , given by (4) expresses the normal velocity on each wave surface and at every point of it, it represents the phase velocity. The velocity of the particle with which we started, is not u but

$$v = \sqrt{\dot{x}^2 + \dot{y}^2 + \dot{z}^2} = \frac{\sqrt{2(E - V)}}{\sqrt{m}}.$$

* Actually the kinetic energy T does not depend directly on the time. If the velocity remains unchanged T is a constant and the variation of the time alone induces in W only the variation $E dt$, so that $\frac{\partial W}{\partial t} = -E$.

We conclude, therefore, that Jacobi's equation (1) may be regarded as representing a phenomenon of wave propagation associated with the moving body, so long as the latter conforms to Newtonian mechanics. On the other hand, all atomic phenomena lead us to think that the laws valid for the motion of very small particles must be more complex than the Newtonian laws. Now we have arrived at the Jacobi equation. By analogy with this and other equations of mathematical physics, the practice is adopted of associating with atomic phenomena, a wave phenomenon which serves merely as a form of statement of the mechanical laws valid for small particles.

We recall that in discussing vibrating mechanical systems, the stretched string and membrane, we met with the general wave equation,

$$u^2 \left[\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right] = \frac{\partial^2 \psi}{\partial t^2} \text{ or } \Delta_2 \psi = \frac{1}{u^2} \frac{\partial^2 \psi}{\partial t^2} \quad (5)$$

where u is the velocity of propagation. It is found that the laws which govern atomic phenomena can also be represented by differential equations of the type (5). Schrödinger has, in fact, succeeded in creating a new mechanics, more general than Newton's, the laws of which are expressed symbolically by equations of the type :

$$H\psi = \frac{h}{2\pi i} \frac{\partial \psi}{\partial t} \quad (6)$$

where H is a suitable *differential operator*. In the simple case of the motion of a particle of mass m and energy E in a field of force derivable from a potential V , equation (6) becomes

$$\Delta_2 \psi + \frac{8\pi^2 m}{h^2} (E - V)\psi = 0 \quad (7)$$

This is an important form of Schrödinger's equation. Just as in the case of the vibrating string, equation (7) leads necessarily to *discrete* values for the parameter E . These are termed *eigenvalues*. The appearance of a discrete set of permissible *eigenvalues* for E is a consequence of the condition that the

equation shall have a solution ψ which is *finite, continuous and single-valued*.

For example, if one considers a particle of mass m and charge e rotating about a stationary particle of charge e (this is the case of the hydrogen atom) the potential function is $V = -\frac{e^2}{r}$. It will

now occur, even to the uninitiated reader, that the special values of the energy E which allow of a solution ψ which is finite, continuous and single-valued in the whole of space, may perhaps be the discontinuous energy values found by Bohr in his theory of spectral lines. As will be seen, this is the case.

Equation (7) takes no account of the variation of mass with velocity, and hence is subject to the restriction—actually not a very serious one—that it ceases to be valid for high velocities of the particle, approximating to the velocity of light. The corresponding equation furnished by relativistic mechanics when account is taken of the variation of velocity with mass, will not be discussed.

In problems of atomic mechanics, the eigenvalues of Schrödinger's equation give the possible values of the energy, that is to say, the energy values of stable states or *quantised states* of the system.

With regard to ψ we shall make the following observations, anticipating later developments. We know that in the theory of light the study of the motion of the photons starts out from the wave equation $\Delta_2\psi = \frac{1}{u^2} \frac{\partial^2\psi}{\partial t^2}$. This equation comprehends not only geometrical optics but also physical optics; ψ represents the *probability* distribution of the photons, and is the scalar whose square gives the luminous intensity.

Similarly, in Schrödinger's equation ψ represents the probability distribution of the particles. Thus no immediate physical reality should be attributed to the ψ waves. It is only in limiting cases corresponding to the transition from physical to geometrical optics, that this *probability* solution of the various problems of atomic mechanics, reduces to the *deterministic* solution of ordinary macroscopic mechanics.

Schrödinger has generalised his equation (7) by supposing ψ related to the time t , by the formula $\psi = ae^{2\pi i\nu t}$. It follows from this that

$$\frac{\partial \psi}{\partial t} = 2\pi i\nu \psi = \frac{2\pi i}{h} E \psi; \text{ hence } E = \frac{h}{2\pi i} \frac{\partial \psi}{\partial t} \frac{1}{\psi}.$$

Substituting this value for E , (7) becomes

$$\Delta_2 \psi - \frac{8\pi^2 m}{h^2} V \psi - \frac{4\pi i m}{h} \frac{\partial \psi}{\partial t} = 0,$$

which remains valid however ψ depends on the time.

The Hydrogen Atom According to Wave Mechanics

As mentioned above, in the hydrogen atom the potential function, corresponding to equal and opposite charges $+e$ and $-e$, is given by $V = -\frac{e^2}{r}$,* so that the fundamental equation becomes:

$$\Delta_2 \psi + 8\pi^2 \frac{m}{h^2} \left(E + \frac{e^2}{r} \right) \psi = 0. \quad . \quad . \quad . \quad (8)$$

The investigation of the regular solutions of the equation leads, just as in the classical problems cited on p. 269, *et seq.*, to *eigenvalues* for the parameter E . These turn out to be the possible energy values of the atom corresponding to Bohr's quantum states.

The method of solving the differential equation for the vibrations of a mass of fluid contained in a sphere, is apparent from our brief summary of the theory of vibrating systems. The solution for the vibration function ψ , which is taken to be the condensation of the fluid in the sphere, is obtained by putting ψ equal to the product $f(r)\Phi(\theta)\Psi(\psi)g(t)$.

The present problem is solved in just the same way. ψ , the function required, is put equal to the product $f(r). Y(\theta, \phi)$, that is, to the product of a function of the radial distance, and a function of the angular position. Omitting details of the calculation, the following two equations are obtained

$$\frac{r}{f} \frac{d^2}{dr^2} (rf) + \frac{8\pi^2 m}{h^2} (Er^2 - e^2 r) = a \quad . \quad . \quad . \quad (9)$$

$$\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} + aY = 0 \quad . \quad . \quad (10)$$

* Observe that in the differential equation r denotes the distance from the nucleus to the field point in space, not to the electron to which no special location must be ascribed. This point will be better understood on p. 305.

where a is a constant. For particulars of the calculation refer back to the problem of the vibrating membrane.

The second of these is a very well-known equation which has *uniform* solutions when and only when a is of the form $l(l+1)$, where l is an integer. When such a value for a is inserted in (9) it appears that the resulting equation has the following properties. If E is negative, regular solutions exist only when E has one of the series of discrete values,

$$E = - \frac{2\pi^2 me^4}{h^2 n^2} \quad n = 1, 2, 3, 4 \dots \quad (11)$$

In the Bohr-Sommerfeld theory we had to deal with the azimuthal and radial quantum numbers which, added together, gave the total quantum number. To Bohr's azimuthal quantum number corresponds our $(l+1)$ and to the radial quantum number our $n - (l+1)$.

This result is very satisfactory. The consecutive values of the energy in the stationary states of the hydrogen atom are confined to those furnished by equation (11) above, and (11) is none other than the equation obtained by Bohr to account for the hydrogen spectrum.

Schrödinger's theory had necessarily to lead to this result, for otherwise it would be in conflict with experiment.

Thus, the discontinuity of the stationary states, which until 1924 had constituted one of the most unsatisfactory postulates of the quantum theory, emerges quite naturally from the wave theory in a way precisely similar to that in which the various natural frequencies of a stretched string or a vibrating elastic medium are obtained.

The functions of r met with in this problem resemble Bessel functions, with the difference that they have only a finite number of positive roots, the number of these corresponding to the radial quantum number.

To each value of E there exists a certain set of possible solutions corresponding to different values of the constants in the mathematical problem; these solutions are precisely those of the Bohr theory, associated with different subdivisions of the

total quantum number into azimuthal and radial quantum numbers. It will be recalled that these energy levels, which are equal to each other when the atom exists under normal field-free conditions, separate by small amounts as a consequence of perturbations, such as an applied electric field (Stark effect).

In the state characterised by $n = 1$, $k = \text{zero}$, which corresponds to the first Bohr orbit, the complete vibration system specified by the wave scalar ψ , exhibits spherical symmetry and there are no *nodes*.

For $n = 2$, $l = \text{zero}$, again there is spherical symmetry; the function $f(r)$ associated with the eigenvalue of E , vanishes for a certain value of r and there is a spherical node. This case corresponds to the lowest state of excitation of the atom.

To sum up, between the earlier quantum numbers and the parameters appearing in Schrödinger's equation for hydrogen, the relation,

$$n = n_r + k = n + (l + 1)$$

holds. n_r denotes the radial quantum number or the number of nodes in the radial direction, and $k = l + 1$ is the azimuthal quantum number. It is now readily understood why k cannot be zero. The mathematical explanation is that l , which equals k diminished by unity, can assume only the values from zero to $n - 1$. In Bohr's theory, expressed in terms of the orbits, the view taken was that the orbit of the hydrogen atom could not degenerate into a segment of a straight line when the electron would collide with the nucleus.

Schrödinger's theory leads to the conclusion that the hydrogen atom in its normal state (unexcited) exhibits spherical symmetry. According to the old style model, on the other hand, the hydrogen atom should possess a particular structure plane of the electron orbit and should therefore show plane symmetry.

Experiment fails to support this view. By Gerlach and Stern's method, it is possible to direct the atoms into a non-homogeneous magnetic field where the orbital planes should be arranged parallel one to another. If then a ray of light is passed through the

gaseous mass of atoms orientated in this way, it would be expected that, on account of the difference of structure perpendicular and parallel to the field respectively, the gas would behave optically like a crystal and would show double refraction. This does not occur and hence the spherical symmetry of the atomic field as required by wave mechanics is established.

The same thing is shown by experiments on the canal rays of hydrogen, which in a magnetic field have the same free path whether they are made to travel in the direction of, or perpendicular to the magnetic field (Fraser's experiment). This proves that the electric field of the atom, on which *collisions* with other atoms depend, is the same in all directions.*

Wave Mechanics of the Stark Effect

In discussing the theory of the Stark effect given by Sommerfeld and Epstein, we have seen that when the hydrogen atom is situated in a powerful electric field F , its spectrum is much richer in lines than when the atom is in the normal state. This is so because, whilst for the atom in the normal state the different electron orbits corresponding to the same total quantum n all have the same energy E (so that in the passage of the electron from one to another there is no emission of radiation), when the electric field F is applied, every orbit is deformed and acquires additional energy of amount given by the celebrated Epstein formula :

$$\Delta E = \frac{3Fh^2n}{8\pi^2me} k$$

Thus, when the atom is in an electric field, orbits of different eccentricities, *i.e.*, of different azimuthal quantum numbers k , but with the same total quantum number n , possess different energies and are capable of giving rise to spectral lines. It will be recalled that the number of different orbits into which the Bohr orbit of total quantum number n separates, equals exactly n , as the possible values of the azimuthal quantum number are given by 1, 2, 3. . . . n . The stationary state of total energy $E = 7h\nu$,

* Fraser, *Proc. Roy. Soc. A.*, 114, 1927.

for example, subdivides under the influence of the field into seven different states.

In wave mechanics, to determine the waves associated with the electron subjected to an electric field of intensity F , the potential energy of the electron must be introduced. This is equal to $-\frac{e^2}{r} + eFz$, where z is displacement measured in the direction of the field. Inserting this value for V in Schrödinger's equation, one obtains :

$$\Delta^2\psi + \frac{8\pi^2m}{h^2} \left(E + \frac{e^2}{r} - eFz \right) \psi = 0$$

m = mass of the electron.

e = charge of the electron.

To solve this equation, it is convenient to transform from rectangular to parabolic coordinates (see p. 118). Completing the solution on the usual lines, the calculations give the frequency of the associated waves, and the nodal paraboloids, double cones and spheres. For the eigen energies are obtained precisely the same values as furnished by Epstein's calculations.

Thus the problem of the Stark effect examined by the methods of wave mechanics leads to the same conclusions as those previously arrived at by Epstein on the basis of the older quantum theory. The application of the field F introduces a multiplicity of vibrating systems which correspond uniquely with the various separate orbits mentioned above.

Not only the energy levels, and hence the frequencies, but also the intensities and the polarisations of the radiation emitted in the Stark effect, have been calculated, in complete agreement with experiment.

Other Examples of Wave Mechanics

The Oscillator. By an oscillator is understood a particle, say an electron, which vibrates about its equilibrium position. The oscillator is *harmonic* if the motion is expressible by the sine law. It will be recalled that Planck, in 1900, started out from the consideration of the oscillator in explaining the law of radiation

a *black body*, postulating that the vibrational energy was an integral multiple of the frequency ν multiplied by the constant h , so that energy variations could occur only in steps of amount $h\nu$. Twenty-five years later, Schrödinger's theory furnished an explanation of this mysterious postulate, although the new result is not in complete agreement with that of the older quantum theory. In this case, as in others, it is the wave mechanics conclusion which accords better with experiment. The equation of the oscillator is given by :

$$x = A \sin (2 \pi \nu t),$$

that the instantaneous velocity $v = A2\pi\nu \cos (2\pi\nu t)$. The kinetic energy has the value $L = 2A^2\pi^2\nu^2m \cos^2(2\pi\nu t)$. The total energy E is obtained immediately by observing that when the vibrating particle is at the mid-point of its trajectory, passing through the equilibrium position, the kinetic energy is a maximum and the potential energy is zero. L is a maximum when $2\pi\nu t$ is any, so that $E = 2A^2\pi^2\nu^2m$. Subtracting L from E gives the potential energy $V = 2\pi^2\nu^2mx^2$.

Schrödinger's equation becomes, substituting for V ,

$$\frac{\partial^2\psi}{\partial x^2} + \frac{8\pi^2m}{h^2} (E - 2\pi^2\nu^2mx^2)\psi = 0.$$

It can be shown that the eigen values of the above equation are all added in,

$$E = (2n + 1) \frac{h\nu}{2}, \text{ where } n = 1, 2, 3 \dots$$

that the energy of the oscillator can assume only the series of discrete values :

$$\frac{1}{2} h\nu, \quad \frac{3}{2} h\nu, \quad \frac{5}{2} h\nu, \dots$$

In Schrödinger's wave mechanics the energy of a linear harmonic oscillator is an odd integral multiple of the *half* energy element,

this result differs from that of the older quantum theory which

led to integral multiples of $h\nu$. That it was necessary to introduce the half quantum in interpreting molecular spectra, had already been discovered before Schrödinger put forward his theory.

It follows from Schrödinger's calculation that the lowest energy the oscillator can assume, is not zero but $\frac{h\nu}{2}$. Now physical theory attributes the heat energy of a body to oscillations of the atoms about their equilibrium positions. Various discrepancies between the original quantum theory and the results of certain low temperature measurements, had, a few years previously, led certain physicists—in particular, Nernst—to the hypothesis that the energy of a body at the absolute zero of temperature, has still a finite value different from zero. It is now seen that this assumption is a natural consequence of Schrödinger's mechanics.

Rotator with Free Axis. By a rotator is understood a dumbbell shaped body consisting of two spheres connected together with a slender rod. The system is supposed incapable of rotation about the axial line, but it can assume any orientation in space, the latter being specified by two angles θ and ϕ . The motion is similar to that of a particle moving about a fixed centre and at a constant distance therefrom, and this fact is made use of in solving Schrödinger's equation.

The *dumbbell* rotator serves as a suitable model for the molecules of diatomic gases such as O_2 , H_2 , N_2 , etc. The energy being wholly kinetic, the term V representing the potential energy in Schrödinger's equation, disappears and the equation reduces to :

$$\Delta\psi + \frac{8\pi^2 EI}{h^2} \psi = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where I is the moment of inertia of the system.

Expressing Δ in polar co-ordinates, we obtain :

$$\operatorname{cosec} \theta \left[\frac{d}{d\phi} \left(\operatorname{cosec} \theta \frac{d\psi}{d\phi} \right) + \frac{d}{d\theta} \left(\sin \theta \frac{d\psi}{d\theta} \right) \right] = - \frac{8\pi^2 EI}{h^2} \psi \quad . \quad (2)$$

The function ψ being single valued must return to its original value when the angles θ and ϕ vary by a multiple of 2π . For this

to occur, it can be shown that the energy is necessarily equal to one of the discrete series of values defined by the equation,

$$\frac{8\pi^2 EI}{h^2} = n(n+1) \quad \text{where } n = 0, 1, 2, 3 \dots \quad (3)$$

We wish now to introduce into this equation the moment of momentum $U = mrv$ which is related to the energy E of the mass point, by the equation $m^2 r^2 E = \frac{1}{2} U^2$. The moment of inertia I has the value $I = mr^2$. Substituting for E and I in (3), the moment of momentum can have only the values,

$$U = \frac{h}{2\pi} \sqrt{n(n+1)} \dots \dots \dots (4)$$

Again Schrödinger's theory diverges a little from the original quantum postulate of Bohr, which asserts the condition $U = mvr = n \frac{h}{2\pi}$. We note particularly the reappearance of *half quantum numbers*, for $n(n+1) = (n + \frac{1}{2})^2 - \frac{1}{4}$, so that the difference between two energy states corresponding to the quantum numbers n_1 and n_2 is given by,

$$E_1 - E_2 = \frac{h^2}{8\pi^2 mr^2} [(n_1 + \frac{1}{2})^2 - (n_2 + \frac{1}{2})^2]$$

in place of,

$$E_1 - E_2 = \frac{h^2}{8\pi^2 mr^2} (n_1^2 - n_2^2)$$

the value yielded by the earlier quantum theory.

However, it is now recognised that the physics of the atom is governed by quantum (wave) mechanics and for that reason the results furnished by Schrödinger's equation are exact whereas those of the old theory (Bohr and Sommerfeld) represent only approximations.

The Free Electron in Wave Mechanics

An electron moving in a field-free space has kinetic energy $E = \frac{1}{2}mv^2$ and potential energy V equal to zero. Such an electron

moves in a straight line. If V is put equal to zero in Schrödinger's equation, we obtain :

$$\frac{\partial^2 \psi}{\partial x^2} + \frac{8\pi^2 m E}{h^2} = 0 \quad \text{where } E = \frac{1}{2} m v^2.$$

The partial derivatives with respect to y and z are zero, because the problem is essentially one-dimensional, and the co-ordinates are chosen with the x -axis parallel to the direction of motion of the electron. The wave associated with the electron has frequency,

$$\nu = \frac{E}{h} \text{ and wave length } \lambda = \frac{E}{\sqrt{2mE}} \bigg/ \frac{E}{h} = \frac{h}{mv},$$

which is obtained by dividing the velocity of propagation by the frequency.

If account is taken of the variation of mass with velocity (*i.e.*, allowing for the modification required by relativity) the general relation arrived at, is

$$\lambda = \frac{h}{p}$$

where p is the momentum of the particle. This formula is also valid for light quanta having energy $E = h\nu$. In fact to obtain the correct value of the momentum which is associated with every luminous radiation, and which is evidenced in the mechanical pressure of light, it is necessary to define the momentum of a light quant by the relation :

$$p = \frac{h\nu}{c}.$$

Combining this with the preceding result, gives the identity :

$$\lambda = \frac{h}{h\nu/c} = \frac{c}{\nu}.$$

We may say that in the same way as the quantum theory of light ascribes to the wave of frequency ν , energy concentrated into corpuscles of amount $h\nu$ (having momentum $\frac{h\nu}{c}$), so wave mechanics relates the motion of a particle of velocity v , with the propagation of a wave of wave-length $\lambda = \frac{h}{\text{momentum}}$.

For electron velocities such as are met with in discharge tubes, the corresponding wave-lengths λ are of the same order of magnitude as X-ray wave-lengths, as is seen immediately by substituting for m and v their numerical values. For example, a "150 volt" electron is associated with a wave-length λ of about 1 Ångström unit.

The coincidence may suggest that if a stream of electrons were projected onto a crystal, the procedure adopted in the diffraction of X-rays, diffraction would take place, in the sense that the electrons would be thrown back from the surface as if the phenomenon consisted of the reflection of waves, just as in Laue's experiments. Actually there was no more justification for expecting this to occur than there is for expecting to see the x and y of an algebraic equation materialise before our eyes.* Nevertheless, as we shall show, the fact is that everything takes place as though the de Broglie waves, with their wave-length $\lambda = \frac{h}{mv}$, were subject to diffraction by the crystal and represented an actual wave phenomenon. The fall of potential used to set the stream of electron in motion must be of the same order of magnitude as that used to produce X-rays.

The effect in question was shown to occur in the astonishing experiments of Davisson and Germer (1927), and the wave-length derived from diffraction in crystals is exactly that required by the de Broglie Schrödinger theory.

Before going on to describe the now celebrated experiments of Davisson and Germer, we shall amplify a little our discussion of the fundamental bases of Schrödinger's mechanics, as much that has been said can only have left a confused picture of the theory and its implications.

The Starting Point of Schrödinger's Theory and the Original Idea of de Broglie

Up to now, in the main only one aspect of wave mechanics has been developed, namely its ability to yield a calculation of the stationary states, and we have not discussed the origins of the

* Darrow.

theory. The reader will naturally inquire why these unreal waves applied to the mechanics of the microcosm of the atom, and satisfying the fundamental equation, do in fact serve to solve the various problems. Nor has it been stated up to now whether ψ has any physical significance.

The parent idea from which Schrödinger began, was the analogy between the laws of geometrical optics and the classical mechanics of particles. Consider a group of light waves confined to a restricted region of space, which for simplicity may be regarded as a point. This group of waves may be emitted by a projector fitted with a shutter which allows the light to escape during a very short interval of time, for example 10^{-9} sec. If the refractive index of the medium in which the little cylinder of emitted light moves, is variable from point to point, the group will not be propagated with uniform velocity in a straight line, but will move along a curvilinear trajectory determined by Fermat's principle.

It will be recalled that geometrical optics is based on the law of rectilinear propagation, the laws of regular reflection and refraction, and in addition, on the principle enunciated by Fermat in about the year 1650. This principle states that the time of transit of light between any two points A and B, shall be a maximum or a minimum. Expressed analytically, the condition takes the form :

$$\delta \int_A^B n ds = 0$$

where n is the refractive index.

Similarly, in mechanics the trajectory of a particle in a field of force of potential V is determined from the *principle of least action*, enunciated by Maupertuis* about the year 1740, which states that :

$$\delta \int_A^B m v ds = 0 \quad \text{or} \quad \delta \int_A^B \sqrt{2(E - V)} ds = 0$$

(E is the total energy).

Moreover, just as the velocity v of the moving particle at each point of its trajectory is determined as a function of V by the kinetic energy theorem, so the velocity of the group of waves is regulated at each point by the relation which connects the index

* And stated in its precise form by Euler.

of refraction n and the frequency, and it is possible, as we shall see, to substitute for the field of force of potential V , a distribution of refractive index such that the motion of the group of waves is identical with that of the particle.

The analogy just explained applies to geometrical optics rather than to actual physical optics. The fundamental concept in mechanics is that of the trajectory of a material particle, which corresponds to the concept of the *ray* in the optical analogue. The latter, however, is completely defined only in abstract theoretical geometrical optics, and almost completely loses its significance in actual physical optics when the dimensions of the beam of light, or of the obstacles which it encounters in its path, become comparable in size with the wave-length. The phenomena of diffraction make this perfectly clear to us. To anybody acquainted only with geometrical optics, the spreading out of the light which has passed through a small aperture, as actually occurs, would remain quite unintelligible. It may also be pointed out that the notions which are fundamental in physical optics—wave-length, frequency, equation of propagation—do not enter at all into geometrical optics.

In physical optics the significance of the ray is lost whenever experiments are made with objects of dimensions comparable with the wave-length. In the same way, in the mechanics of electrons and atoms the concept of trajectory seems to break down in those cases where the dimensions of the mechanical orbits or their radii of curvature are of the same order of magnitude as the wave-lengths associated with the particles.

Now, comparing these two significant facts, we are tempted to inquire whether the inapplicability of ordinary mechanics to atomic problems may not be of exactly the same character as the inapplicability of geometrical optics to diffraction and interference phenomena, and whether the same method may not be employed to overcome the difficulty.

When the data of an optical problem include lengths (diameters of apertures, etc.) comparable with the wave-length, the simple laws cease to apply. Something of the same kind is found in mechanics when the laws of macroscopic phenomena prove

themselves inadequate to explain the behaviour of extremely small or atomic systems.

Consider, as an example, the rectilinear motion of an electron of velocity v , in a field-free space. The associated wave system has wave-length $\lambda = \frac{h}{mv}$. Now, to answer the question whether an electron moving round in an elliptical orbit of atomic dimensions can be treated by the methods of ordinary mechanics, we observe that if a is an axis of the orbit, $\frac{\lambda}{a} = \frac{h}{mva}$, and (mva) is the quantity

which for the circular trajectory Bohr puts equal to $\frac{h}{2\pi}$, in order to obtain the radius of the quantised orbit of the hydrogen atom in its normal state. Thus $\frac{\lambda}{a} = 2\pi$, and hence $\frac{\lambda}{a}$ is of the order unity.

It is quite clear, therefore, that Newtonian mechanics will no longer be applicable to such an orbit, just as geometrical optics is inapplicable to the diffraction of light due to a disc of diameter a equal to the wave-length of the light, λ .

We return to the point raised above, that it is possible to construct a dispersive medium capable of representing, in conjunction with a group of waves ψ , the kinematical and dynamical characteristics of the motion of a mass m in any conservative field of force of potential V . The dispersive medium is defined by its refractive index at each point, for we know that the reciprocal of the refractive index is proportional to the velocity of propagation $\left(\frac{1}{n} = \frac{u}{c}\right)$, or, to be exact, to the *phase velocity* u .

The oscillations of ψ are propagated in space, subject to the differential equation :

$$\Delta_2 \psi = n^2 \frac{\partial^2 \psi}{\partial t^2} = - \frac{4\pi^2 \nu^2}{u^2} \psi^2 \quad . \quad . \quad . \quad . \quad (1)$$

Now, if the refractive index n is related to the potential $V = f(x, y, z)$, by the equation :

$$\frac{n}{c} = \frac{\sqrt{m}}{E} \sqrt{2(E - V)} \quad . \quad . \quad . \quad . \quad (2)$$

it follows immediately that with this law of dispersion, the velocity v with which the group of waves is propagated, is given by,

$$\frac{\sqrt{2(E - V)}}{\sqrt{m}} \dots \dots \dots (3)^*$$

* Since $\frac{c}{v} = \frac{d}{dv}(n\nu)$, (3) follows from (2).

It is necessary at this point to distinguish carefully between *phase velocity* and *group velocity*. A wave train or group (or wave packet) consists of a collection of waves with frequencies contained within the interval $(\nu - d\nu)$ and $(\nu + d\nu)$. This group advances with the velocity v defined by :

$$\frac{c}{v} = \frac{d}{dv}(n\nu)$$

and the wave process is localised in a small zone of space in as much as, in front and behind, the different waves interfere or cancel out. The phase velocity, on the other hand, is $\frac{c}{n}$, and coincides with the group velocity only if n is constant, *i.e.*, if the medium is non-dispersive.

It is on account of the difference between group and phase velocity in a dispersive medium, that Foucault's rotating toothed wheel method (Vol. I, p. 32) fails to give the true value of the velocity of light in water. For radiation of wave-length $\lambda = 0.5$ micron—for which the refractive index is 1.33—the method gave 221,000 kilometres per second for the velocity of light in water, the true value being 225,000 kms./sec.

To Stokes, Gibbs, and more especially to Lord Rayleigh, is due the explanation of this discrepancy. Each time the luminous pencil is cut off by the interrupter (toothed wheel or rotating mirror), the observable velocity of propagation of the wave train—the *signal*—is not $\frac{c}{n}$, but

$$v = \frac{\text{phase velocity}}{1 + \frac{\nu}{n} \frac{dn}{dv}} = \frac{\text{phase velocity}}{1 - \frac{dn}{d\lambda} \frac{\lambda}{n}} = \frac{c}{n - \frac{dn}{d\lambda} \lambda}$$

It is known that $R = -\frac{dn}{d\lambda} \frac{\lambda}{n}$ is a small quantity (for water $R = 0.018$), and hence we may write: $v = \text{phase velocity} \times (1 - R)$. In this way the difference between the value obtained experimentally, 221,000, and the true value, 225,000 km./sec., is explained.

The expressions given above can also be put in the following form, which is obtained directly from the simple theory based on the superposition of the waves constituting the *group* :

$$v = \frac{\frac{1}{T_1} - \frac{1}{T}}{\frac{1}{\lambda^1} - \frac{1}{\lambda}} = \frac{d\left(\frac{1}{T}\right)}{d\left(\frac{1}{\lambda}\right)} = \frac{d\nu}{d\left(\frac{n\nu}{c}\right)}$$

so that finally :

$$\frac{c}{v} = \frac{d}{d\nu}(n\nu)$$

as quoted at the commencement of this note. It is, of course, necessary to know how n depends upon ν before the differentiation can be carried out.

and this expression is identical with that representing the velocity of a particle of energy E in a field of potential V , as deduced from the equation $\frac{1}{2}mv^2 = E - V$.

In a similar way it can be verified that not only the velocity but also the trajectory of the wave group coincides with that of the particle.

Here we see the relation between the propagation of the ψ waves, and the motion of the particle from which—mathematically—they originate. The waves travel with the phase velocity u , whereas the associated particle has a velocity equal to the group velocity of the waves. When, however, the size of the orbit or the radius of curvature is very small, the “wave packet” is diffracted, scattered in all directions, away from the zone of the orbit.

It follows that micro-mechanical problems can be studied in detail only by employing the equation of wave propagation. It must not be forgotten, however, that these ψ waves do not carry energy, and hence the function ψ is to be considered as an auxiliary mathematical function which in itself has no physical significance. We shall explain on p. 304 the significance to be attached to the *square* of the amplitude, $\psi\bar{\psi}$. This square represents a probability, so that ψ functions in a similar way to the light vector of optics.

** We wish now to show in what range an optical phenomenon is describable in terms of geometrical optics and in what range the equivalent mechanical problem is describable in terms of classical mechanics.*

We consider a particular solution of Schrödinger's equation, $\psi = \psi_0 e^{\frac{2\pi i}{h}(Et + S)}$, where S is a function of position only, i.e., it depends only on x , y and z . Substituting this value of ψ in Schrödinger's equation, and dividing throughout by ψ/h^2 , we obtain,*

$$2\pi i h \Delta_2 S - 4\pi^2 (\text{grad } S)^2 + 8\pi^2 m(E - V) = 0 \quad . \quad . \quad . \quad (\alpha)$$

When $h \Delta_2 S$ is small compared with $\Delta_1 S$, (α) becomes :

$$\Delta_1 S = 2m(E - V),$$

which is merely the Hamilton-Jacobi equation representing the

* Since $\frac{\partial \psi}{\partial x} = \frac{2\pi i}{h} \psi \frac{\partial S}{\partial x}$; $\frac{\partial^2 \psi}{\partial x^2} = -\frac{4\pi^2}{h^2} \left(\frac{\partial S}{\partial x}\right)^2 \psi + \frac{2\pi i}{h} \psi \frac{\partial^2 S}{\partial x^2}$.

motion of a point in ordinary mechanics. S denotes the *action* (see p. 274).

Thus for the approximate validity of geometrical optics $h\Delta_2 S$ must be small, and this cannot be the case if the particle is constrained to move in a restricted space.

It may be concluded :

(a) That Schrödinger's equation represents the laws of motion of a particle, over a more extended range of the variable parameters than do the ordinary equations of dynamics.

(b) That, in the particular case just considered, the common range in which the latter coincide with the more general equation corresponds to $h\Delta_2 S$, being very small compared with $\Delta_1 S$.

The microcosm of the atom is not included in the common range, and for it, classical mechanics are not applicable, just as geometrical optics ceases to be valid when objects of size comparable with the wave-length are interposed in a beam of light and give rise to diffraction phenomena.

(c) The trajectory of a moving particle can be looked upon as a simplified model in wave mechanics, just as rays of light serve as simplified models in physical optics.

It is easy to show* that Sommerfeld's quantum conditions,

$$\int p dq = nh,$$

are contained as a first approximation in Schrödinger's equation.

* For, when "geometrical optics" is valid, Schrödinger's equation admits of a solution of the form

$$\psi(x, y, z, t) = \psi_0 \cos \frac{2\pi}{h} (Et + S),$$

in which S is the action, $\int dS = \Sigma \int p dq$. As the function ψ is single-valued at all points of space, the phase $\frac{2\pi}{h} (Et + S)$ must change in passing round a closed contour by an exact multiple of 2π . Hence $\int dS = nh$. Furthermore, in multiperiodic systems in which the variables are separable, the condition $\Sigma \int p dq = nh$ is known to be equivalent to Sommerfeld's conditions :

$$\int p_1 dq_1 = n_1 h \quad \dots \quad \int p_2 dq_2 = n_2 h.$$

We shall now explain briefly the original idea which formed the germ of Schrödinger's theory. In 1924 Louis de Broglie conceived the idea of associating with every material particle (atom, electron, proton) a wave process consisting of a train of waves of frequency ν such that the corresponding energy $h\nu$ equalled the energy of the particle, defined according to relativity theory, *i.e.*, such that

$$h\nu = mc^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

In saying that this train of waves accompanies the particle moving with velocity v , it is meant that the group velocity of the wave train coincides with v , and, as the phase velocity u has not previously been considered, it must now be assigned in such a way that this is the case. The condition u has to satisfy turns out to be,

$$uv = c^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In fact, the group velocity is then given by

$$\frac{1}{\text{group velocity}} = \frac{d\left(\frac{\nu}{u}\right)}{d\nu} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The frequency ν is related to ν_0 , the frequency referred to a system of co-ordinates rigidly attached to the moving particle, by the equation,

$$\nu = \frac{\nu_0}{\sqrt{1 - \frac{v^2}{c^2}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and we obtain from (2), (3) and (4),

$$\frac{d\left(\frac{\nu}{u}\right)}{d\nu} = \frac{v}{c^2} + \frac{\nu}{c^2} \frac{dv}{d\nu} \quad \text{and} \quad \frac{d\nu}{dv} = \frac{\nu_0 v}{c^2 \left(1 - \frac{v^2}{c^2}\right)} = \frac{\nu v}{c^2 - v^2}.$$

Hence,

$$\frac{1}{\text{group velocity}} = \frac{d\left(\frac{u}{\nu}\right)}{d\nu} = \frac{v}{c^2} + \frac{c^2 - v^2}{c^2 v} = \frac{1}{v}.$$

The group velocity is therefore equal to that of the moving

particle, which is accompanied by a wave whose maximum amplitude coincides in position with the particle at every instant.

To find the wave-length λ associated with the particle, it is only necessary to use the relations $u = \lambda\nu$, $h\nu = mc^2$, $uv = c^2$ to obtain,

$$\lambda = \frac{h}{mv}.$$

The Diffraction of Electrons by a Nickel Crystal (Davisson and Germer).^{*} Diffraction of Electrons by Thin Films (G. P. Thomson)

From de Broglie's theory it follows that with a moving particle is associated a wave process. With this idea a new phase of physical theory commenced and a corresponding field of experimental research has been opened up. In the latter belong the experiments of Davisson and Kunsman[†] and, more recently, those of G. P. Thomson, Davisson and Germer, Rupp[‡] and Kikuchi.[§]

The present section will be devoted to a discussion of this work.

The intensity of the reflected pencil obtained by projecting a stream of electrons of known variable velocity on to a crystal of nickel was measured as a function of direction by C. Davisson and L. H. Germer. The crystal was cut parallel to the lattice plane, 111, *i.e.*, along the octahedral face, and the bombardment was applied perpendicular to the surface. (Nickel exhibits *face centred cubic* structure.)

The electrons, which suffer little or no loss of velocity, are diffusely reflected in all directions, but it is found that for certain critical electron velocities and for certain directions of reflection, reflected pencils of exceptional intensity occur.

Wave mechanics asserts—as has been shown—that with an electron of velocity v is associated an undulatory process of wave-length $\lambda = \frac{h}{mv}$, where m is the mass of the electron. Now as the

^{*} *Phys. Rev.*, 30, p. 705, 1927. *Proc. Nat. Acad. Sci.*, 14, p. 317 and p. 619, 1928. *Phys. Rev.*, 31, p. 305 and p. 708, 1928.

[†] Davisson and Kunsman, *Proc. Amer. Acad.*, 22, 1923.

[‡] Rupp, *Ann. d. Physik*, 85, p. 981, 1928. Also 1, p. 773, 1929.

[§] Kikuchi, *Japan. Journ. of Physics*, 5, p. 83, 1928.

lattice spacings of the nickel are known, it is easy to determine the directions in which a beam of X-rays would be reflected by the different lattice planes in the crystal. The highly important result of the experiments with electrons is that the special directions of reflection referred to above, coincide with those which would be obtained by employing X-rays of wave-length $\frac{mv}{h}$. In fact, they are identical with the directions of the Laue pencils which

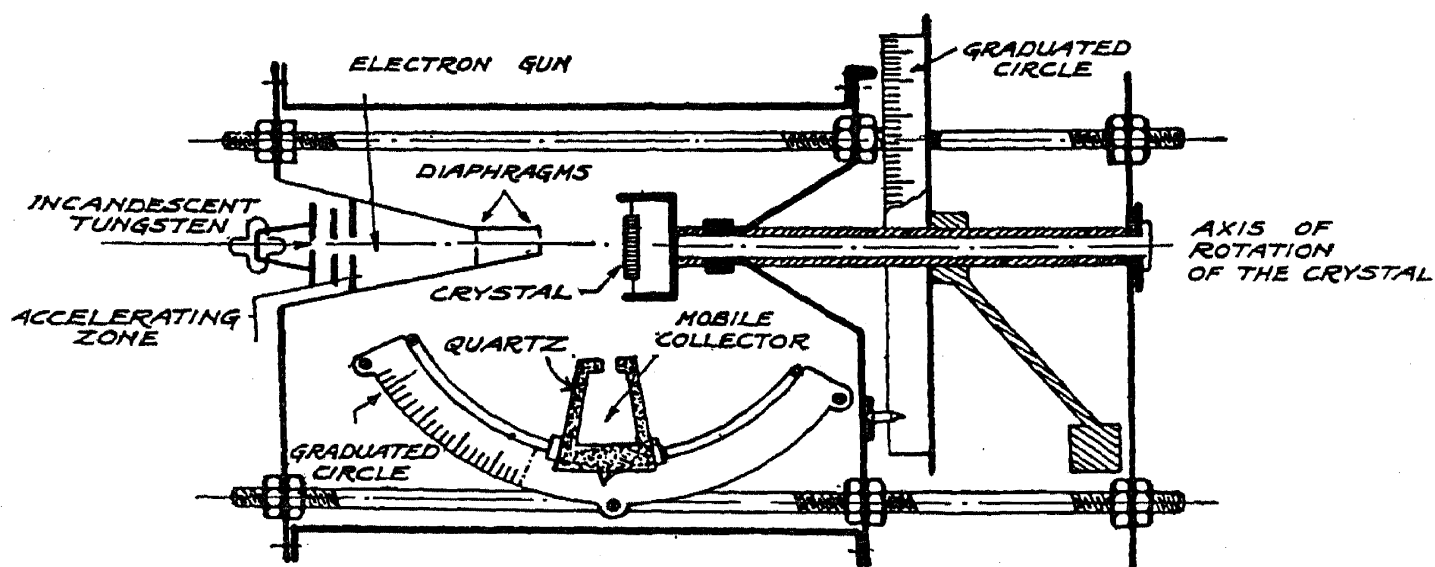


FIG. 67.—Davisson's apparatus.

would be obtained from the crystal with X-rays of equivalent wave-length, the equivalence being defined by the relation $\lambda = \frac{h}{mv}$.

This result had been predicted by Elsasser in 1925, immediately after the appearance of L. de Broglie's first speculations.

Davisson's apparatus comprises the so-called *electron gun*, the crystal and a collector. The electrons are emitted thermally from an incandescent tungsten filament. After being accelerated in an electric field and delimited by suitable apertures to form a fine parallel pencil, they traverse a space free from electric force, impinge on the crystal, and after reflection arrive finally in the collector.* The electrons fall normally on to the nickel plate, and

* As no electric force, except the accelerating field, must act on the electrons, the outside wall of the canon, the crystal, the collector and the box which contains the whole apparatus are all maintained at the same potential. The accelerating potential in Davisson and Germer's experiments varied from zero to 370 volts.

those which, after reflection, pass through the small aperture in the collector, are detected by the aid of a sensitive galvanometer. The area bombarded amounts to a few square millimetres. The angle between the incident direction and the line joining the point of impact to the collector can be varied, and the crystal itself can be rotated about the incident direction as axis.

The nickel disc possesses a well-marked crystalline structure induced by drawing and annealing, and the orientation of the larger crystals is determined by examination of the optical reflections from facets formed by etching. To prepare the desired facet a cut is made so as to have a smooth face parallel to the lattice plane 111 , *i.e.*, a face perpendicular to a diagonal of the cube, and it is this triangular facet so prepared which is exposed to the bombardment incident normally to the surface (see Fig. 68).

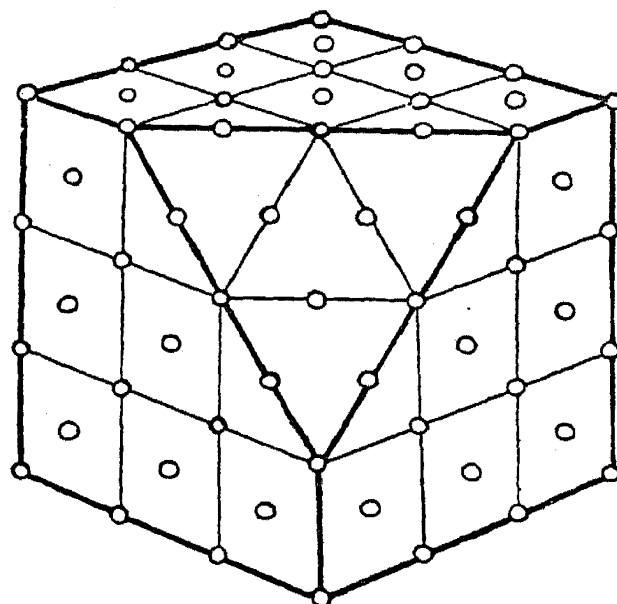


FIG. 68.

The determination of the orientation of the facet under test is accomplished using a spectrometer, with a crystal goniometer in place of the prism. From the setting of the collimator and crystal goniometer, the orientation of the surface being examined is determined.

The complete study of the directions in space along which the electrons are reflected by the crystal involves changing the bombarding potential, and the altitude and azimuth of the collector, or, rather, two of these quantities are kept constant and the third is varied.

We pass over the complicated details of the experiments, and merely quote an example. With a bombarding potential of 54 volts a well-marked reflection at an angle of 50° is obtained. Fig. 69 illustrates the general arrangement of the experiment. By varying the azimuth and the altitude of the collector, the entire

solid angle about the incident direction is explored. Fig. 70, which needs little explanation, shows the current of the collector at various azimuths, with a fixed accelerating potential of 54 volts and fixed altitude, $\theta = 50^\circ$. The very high current at certain angles is well brought out in this diagram, and it will be noted

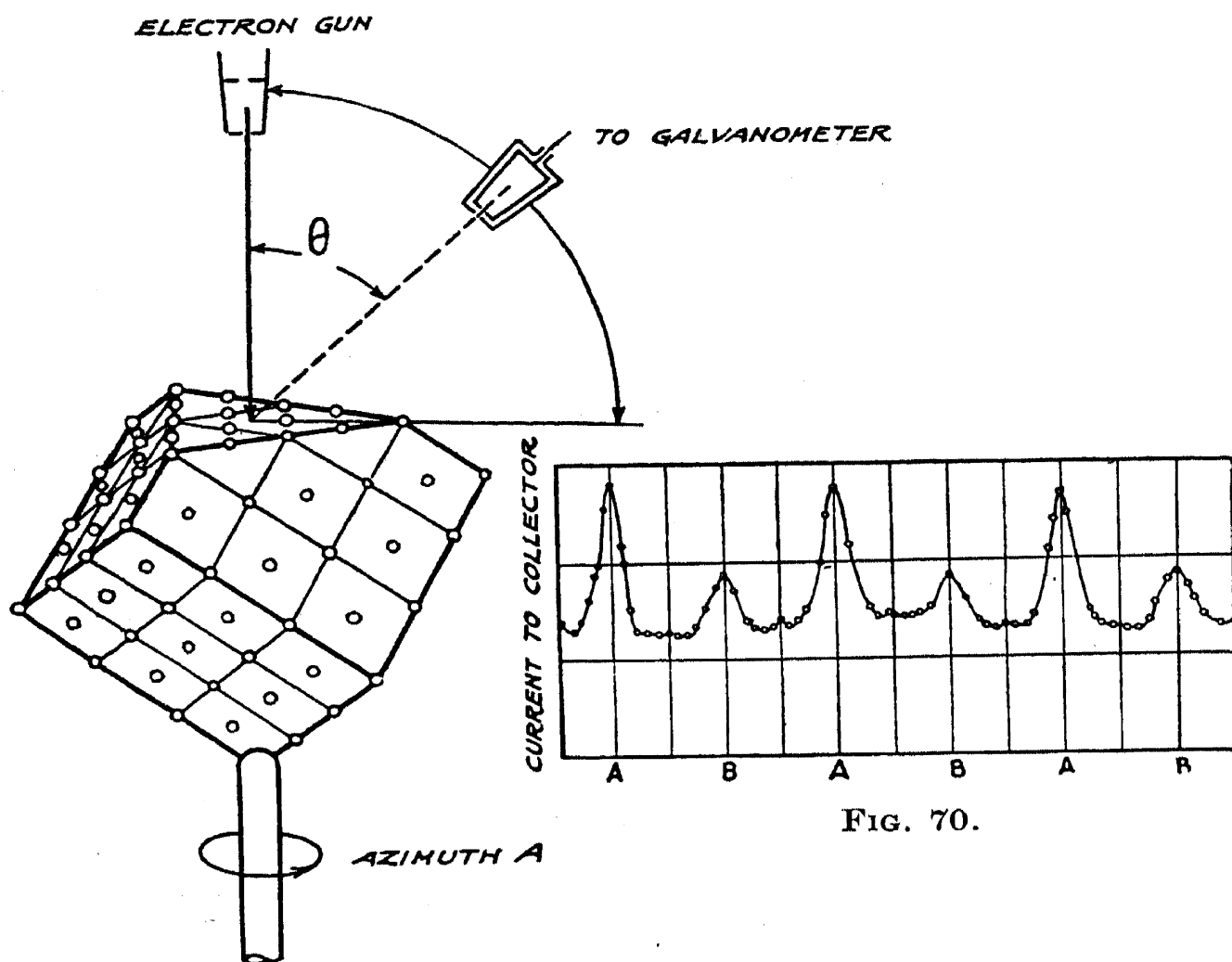


FIG. 69.

FIG. 70.

that main current maxima occur at three angles in agreement with the ternary symmetry of the crystal axis concerned.

Assuming, for the moment, the wave-length *associated* with the electrons to be given by $\lambda = \frac{h}{mv}$, it follows from the known relation between the velocity v and the bombarding potential V , that,

$$\lambda = \left(\frac{150}{V} \right)^{\frac{1}{2}} \quad \begin{array}{l} \lambda \text{ in \AA ngstr\"om units.} \\ V \text{ in volts.} \end{array}$$

Now it is found that the angle at which electron reflection is greatest coincides with that at which X-rays of wave-length λ give maximum intensity. In other words, the angle θ satisfies Bragg's fundamental equation :

$$n\lambda = d \sin \theta,$$

where d is the distance between the lattice planes. For the (111) plane of nickel, $d = 1.25 \times 10^{-8}$ cm.*

In the experiments just described, the following anomaly was encountered. The electrons were incident normally to the crystal, but the angle of intense reflection of electrons was found not to obey accurately the equation $n\lambda = d \sin \theta$ with $\lambda = \frac{h}{mv}$, which, for simplicity, has been assumed up to now. All the observed angles were slightly different from those deduced theoretically, and the values were such as would be explained if the crystal had been contracted along the normal to the reflecting surface.

Of the three lattice distances, the one not lying in the plane parallel to the external face appeared to be modified, the other two distances being unaffected. This anomaly seemed at first very mysterious, but in 1927 Hans Bethe, of the University of Monaco, gave the correct explanation. The solution lay in Schrödinger's theory itself. The wave-length associated with free electrons of total energy E moving in a space where the potential is V is given by :

$$\lambda = \frac{h}{\sqrt{2m(E - V)}}.$$

Now there exist powerful atomic fields in the interior of the crystal, and these will affect V and hence λ . The wave-length in the crystal (λ) will therefore be different from the wave-length

* For $V = 54$ volts the electrons are reflected most intensely at $\theta = 50^\circ$ and from $\lambda = d \sin \theta$ with $d = 1.25 \times 10^{-8}$ cm., we obtain :

$$\lambda = 1.25 \times 10^{-8} \times \sin 50^\circ = 1.65 \text{ \AA}.$$

The formula $\lambda = \frac{mv}{h} = \sqrt{\frac{150}{V}}$ gives just 1.67 Å.

outside in free space (λ') and the ratio of the two is obviously given by :

$$\frac{\lambda' \text{ vacuum}}{\lambda \text{ crystal}} = \frac{\sqrt{E - V}}{\sqrt{E}} = \sqrt{1 - \frac{V}{E}}.$$

This ratio represents the refractive index n . Now it is the wave-length inside the crystal which obeys Laue's equations for the passage of radiation through the crystal lattice.

For simplicity, we think only of lattice directions not lying in the external surface of the crystal and limit ourselves to a consideration of the fundamental equation $K\lambda = d \sin \theta$. It should be found that the experimental values of θ conform to this equation, if for λ is substituted the wave-length appropriate to the interior of the crystal, *i.e.*, the free space wave-length divided by the refractive index.

The following table shows that this prediction is completely confirmed :

E in volts.	$\lambda \text{ vacuum} = \frac{h}{mv}$	Index n	Corresponding wave-length.
54	1.67 Ångström	0.82	2.03
100	1.22 „	0.82	1.49
138	1.04 „	0.85	1.22
174	0.93 „	0.92	1.01

The potential V , which determines the refractive index, comes out to be about 20 volts.

Other very important experiments,* showing that a wave process is associated with rapidly moving electrons, are those of G. P. Thomson, Professor of Natural Philosophy at Aberdeen University.

The experiments consisted in allowing a homogeneous pencil of cathode rays, *i.e.*, electrons, to impinge normally on an extremely thin film of metal (gold, aluminium) or of celluloid. After passing through the film the electrons were received on a

* See *Roy. Soc. Proc.*, February, 1928.

suitably arranged photographic plate. If the film consists of a large number of minute crystals arranged at random, the figure obtained should be identical with that given by the Debye-Scherrer apparatus (see Vol. I, p. 269), using X-rays of the equivalent wave-length

$\lambda = \frac{h}{mv}$, *i.e.*, a series of concentric rings should be observed. This is, in fact, what occurs.*

The vital condition in the experiment is that the film of matter shall be so thin that an electron, in passing through, is scattered once only. If this condition is not satisfied, the pattern is obscured by the superposition of the deviations, and there appears on the plate a uniform blackening.

The experimental arrangement consisted of a tube in which the cathode rays were generated, and from which they were led through a very fine canal (0.23 mm. diameter) to impinge on the scattering film of gold or aluminium, and then on the photographic plate at a distance of about 30 cm. To establish that the beam

* Combining $\lambda = \frac{h}{mv}$ with $\frac{1}{2}mv^2 = eV$ (where V is the accelerating potential), we obtain :

$$\lambda = h \sqrt{\frac{1}{2meV}} \quad \text{or} \quad \lambda = h \sqrt{\frac{150}{meV}} \quad \dots \dots \dots (1)$$

when V is expressed in volts.

Actually taking into account the variation of mass with velocity the formulæ are modified as follows :

$$\lambda = \frac{h\sqrt{1-\beta^2}}{mv} \quad \dots \dots \dots (2)$$

$$\text{Energy} \quad eV = \frac{mc^2}{\sqrt{1-\beta^2}} - mc^2 \quad \dots \dots \dots (3)$$

$$\text{and hence,} \quad \lambda = h \sqrt{\frac{150}{meV}} \left(1 - \frac{eV}{1,200 mc^2}\right) \quad \dots \dots \dots (4)$$

$$\text{As,} \quad \frac{D}{2} = L \cdot 2\theta \quad \text{and} \quad 2\theta d = n\lambda,$$

$$\text{we obtain,} \quad D = \frac{2n\lambda L}{d} \quad \begin{array}{l} D = \text{diameter of a ring} \\ d = \text{lattice spacing.} \end{array}$$

Thus $\frac{D}{\lambda}$ is constant or,

$$D\sqrt{V} \left(1 + \frac{1}{1,200} \frac{eV}{mc^2}\right) = \text{constant.}$$

G. P. Thomson verified for thin films of aluminium, gold and platinum that this expression remains unchanged on varying the accelerating potential.

used really consisted of electrons moving with equal velocities (homogeneous pencil) Thomson substituted for the photographic plate a willemite screen and deflected the cathode pencil with a magnet. The fact that the fluorescent spot on the screen was displaced as a concentrated spot and was not diffused or spread out into a band, proved the beam to be homogeneous.

The patterns obtained on the photographic plate consisted of series of concentric circles. If these rings are diffraction rings of the Debye-Scherrer type, their diameters D for a given film should vary in such a way that the quantity $D\sqrt{V}$ remains constant,

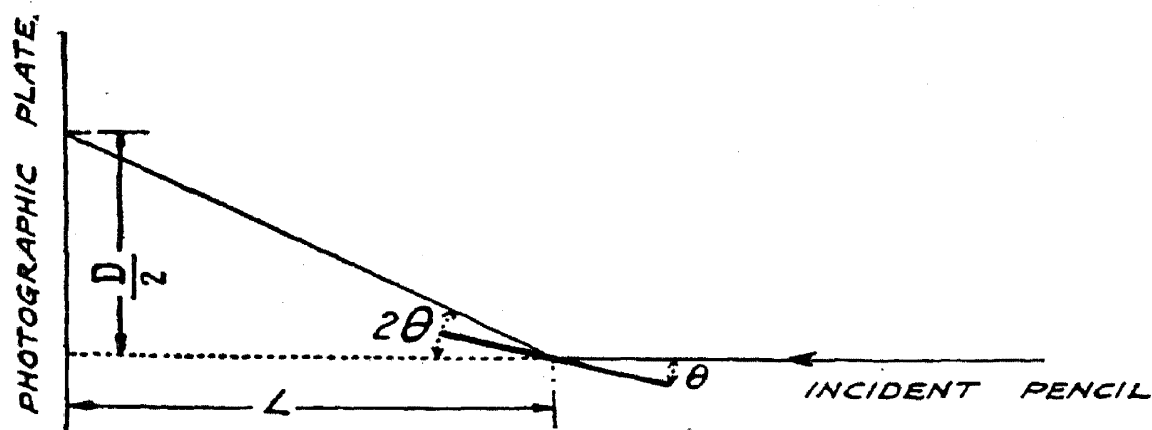


FIG. 71.

where V is the accelerating potential of the cathode rays. We have, in fact, $\lambda v = \frac{m}{h} = \text{constant}$ and $\frac{1}{2}mv^2 = Ve$, so that $\lambda\sqrt{V}$ remains unchanged. Again, λ is proportional to θ ,* and so also is the diameter of the ring. Hence, finally, $D\sqrt{V} = \text{constant}$ (see Fig. 71).

For example, for an aluminium foil, with $V = 30,000$ volts, D equalled 2.45 cm. and the quantity $D\sqrt{V}$ had the same value as with $V = 56,000$, giving a diameter $D = 1.80$ cm. Again for a *gold foil*:

$$\left. \begin{array}{l} V = 24,600 \text{ volts and } D = 2.50 \text{ cm.} \\ V = 54,300 \text{ volts and } D = 1.63 \text{ ,,} \end{array} \right\} D\sqrt{V} = \text{constant}$$

* Since $\lambda = 2d \sin \theta$ for the first order, and 2θ measures the deviation of the incident ray. The diameter of a ring is also proportional to θ . For the small angles involved in the experiments, the angle θ , its sine and its tangent can all be taken as identical.

The thickness of the aluminium films was of the order 10^{-5} cm., and they were obtained by reduction in potash, the gold films being formed by immersion in aqua regia.

If d is the distance between consecutive lattice planes of the cubic crystal of gold, having indices K_1, K_2, K_3 , and a is the cube side then denoting by L the distance from the film to the photographic plate, clearly

$$\frac{D}{2} = 2\theta L = \frac{\lambda}{d} L = \lambda L \frac{\sqrt{K_1^2 + K_2^2 + K_3^2}}{a}.$$

Thus there exists a well-defined relation between the diameter of a ring D and the indices K_1, K_2, K_3 .

Finally, since D, L, λ are known quantities, these experiments can be used to assign for each ring the corresponding value of $\sqrt{K_1^2 + K_2^2 + K_3^2}$,* or, alternatively, having identified the crystal plane, the *absolute value* of a the cube side can be calculated. Thus Thomson found for gold, $a = 3.80 \times 10^{-8}$ cm., while X-rays give $a = 4.06 \times 10^{-8}$ cm.

It will be noted that, in establishing the constancy of $D\sqrt{V}$, the value of a is unimportant, as it is the same for all the rings.

Whereas Thomson used electron rays corresponding to *hard* X-rays, E. Rupp made electron diffraction experiments with slow electrons of from 150 to 320 volts, which were made to pass through thin films. He succeeded in diffracting these slow electrons, using optical gratings and measured accurately the corresponding wave-length. (See *Ann. d. Phys.*, 85—1928, and *Naturwiss*, 16—1928.)

Other workers have continued and developed this type of investigation, among whom may be mentioned Kichuchi in Japan, and Ponte in France,† who obtained for metallic oxides the very clear and well-defined concentric circles predicted by the Debye-Scherrer theory. (See Fig. 72.)

These experiments have for physics an immense importance because they reveal the *double nature* of the electron. The electron

* For example, for one ring $\frac{Da}{2\lambda L}$ was found to equal 2.83, and the face concerned was therefore (2, 2, 0), since $\sqrt{2^2 + 2^2 + 0^2} = \sqrt{8} = 2.83$.

† *Comptes Rendus*, 188, pp. 244 and 909, 1929.

had previously been looked upon as a material element having the attributes of mass, charge, and kinetic energy, and its corpuscular character was represented as the exact opposite of the undulatory mechanism of radiation. The discovery of the undulatory properties of the electron has removed in one step the opposition between the two separate and restricted conceptions. On the other hand, several phenomena which we have met with (photoelectric effect, Compton effect, etc.) had already led to the

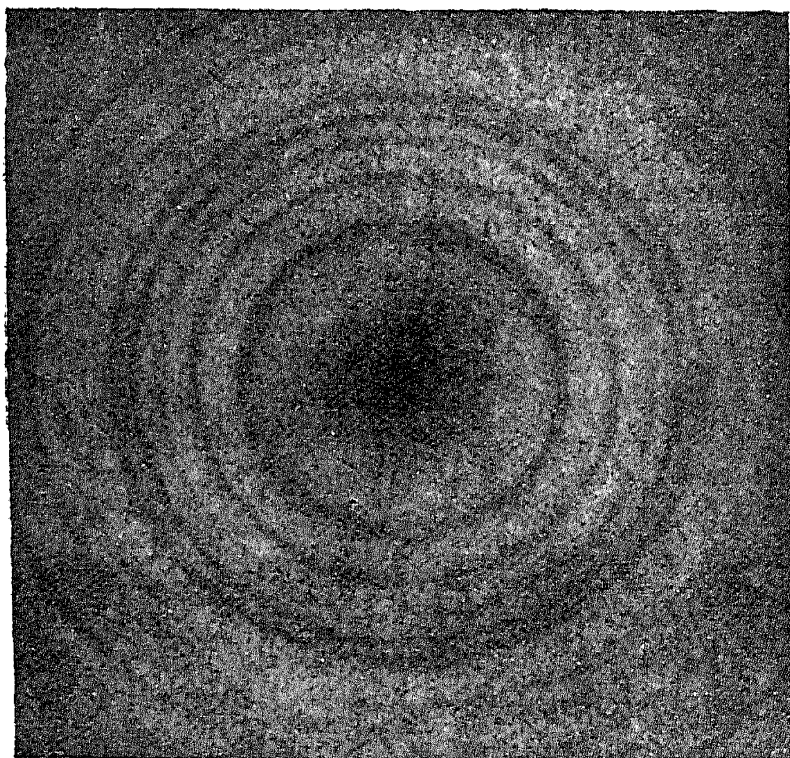


FIG. 72.

view that radiation consisted of groups of photons, or of elements possessing not only energy but also momentum as in the case of material particles. Each of these two species of particle—electrons and photons—exhibits to us properties which we have come to consider as characteristic of matter (mass, momentum), and others such as ordinarily ascribed to radiation (wave-length). The new quantum theory furnishes an explanation of this puzzling state of affairs.

The Physical Significance of the Function ψ

In spite of the rapid consolidation and early successes of the Schrödinger theory, the physical interpretation to be placed on

the vibration amplitude of the scalar ψ has already undergone a change from the form originally suggested by the founder of the theory. At first he had maintained that the square of the amplitude of ψ would represent the *density of electric charge*.* On this view the electron would have a diffuse structure, its electric charge being distributed continuously over a large volume.

The electron, however, in its old character as a centre of charge and mass certainly has a well-established physical reality, demonstrated by innumerable experiments on cathode rays, thermionic electrons, etc. How, therefore, can this point-like structure give place in the atom to a continuous distribution of charge? Again, do not Millikan's experiments, in which an electron is in effect isolated on a minute oil drop, exclude this conception of the electron as an extended vibratory state, and may we not deduce, from the evidence of the Compton effect and the β -ray emission of radioactive substances, the existence of localised charge?

In the wave equation itself, in order to calculate the continuous function ψ for the case of the hydrogen atom, the potential function $-\frac{e^2}{r}$ is introduced, as though the electron were in fact punctiform and not diffuse.

That is to say, although the electron trajectory idea of the old atomic models is abandoned, the point electron is still retained, with the limitation that its precise localisation in space and time ceases to have physical significance.

Born † has shown by arguments which cannot be given here, that *the square of the amplitude of ψ represents the probability* that a system exists in the energy state corresponding to the solution ψ of the fundamental equation. For example, considering an atom with a single electron, ψ is a function of x, y, z, t of the form $\psi = A(x, y, z)e^{-i\omega t}$, and $A^2 = \psi^*$ is the probability of finding the electron at the point x, y, z . In other words, ψ^* tells us how

* If $\psi = A(x, y, z)e^{+i\omega t}$, then $\bar{\psi} = A(x, y, z)e^{-i\omega t}$ and $\psi^* = \psi\bar{\psi} = A^2$.

† Born, *Zeits. f. Physik*, 38, p. 803, 1926.

often the electron passes into a space of unit volume, containing the given point.*

It is clear then that, whether we are dealing with the light quant or the material particle, physics makes use of a single general method—the electromagnetic theory in the former case and the theory of material waves in the latter—which leads to the assignment of a certain magnitude whose square is the probability that the light quant or the electron is situated at the given point of space. The analogy is complete, the simple problem of a single particle, whether of radiation or of matter, is solved. In both cases the notion of trajectory is given up and the theory provides in its place the probability wave.

Thus the new mechanics gives no answer to the question, “How does the particle move?”, but only to the question, “What is the probability that the particle shall be at a selected point, or be travelling in an assigned direction?”

Attention must here be drawn to a fundamental point which tentative interpretations of the function ψ (based on the simplest case, the motion of a single particle in three-dimensional space) have tended to obscure. The argument space of the function ψ , *i.e.*, the assembly of points for which ψ is defined, is in fact not the ordinary space, but the so-called *phase* space which has as many dimensions as there are degrees of freedom in the system considered. For example, for a system of two particles, the phase space is six-dimensional. The attempt to interpret quantum mechanics on the assumption that ψ^* represents the density of electric charge obviously breaks down.

Up to this point we have regarded the system to which Schrödinger's equation is applied as being in a definite energy state, there being no radiation of energy. To investigate the general case in which ψ^* varies with time, the generalised form of the wave equation given on p. 278 must be used.

$$\Delta_2\psi - \frac{4\pi i}{h} \frac{\partial\psi}{\partial t} - \frac{8\pi^2 m}{h^2} V\psi = 0 \quad . \quad . \quad . \quad . \quad (*)$$

* It is clear that the scale of ψ must be so chosen that the total probability is *unity*, or in mathematical language, ψ must be *normalised*.

In this, the parameter representing the energy is eliminated and the equation has solutions corresponding to different energy states. If we continue to accept only such solutions as depend sinusoidally on the time, these will have the form :

$$\begin{aligned}\psi_1 e^{2\pi i \nu_1 t} &= \psi_1 e^{2\pi i \frac{E_1}{h} t} \\ \psi_2 e^{2\pi i \nu_2 t} &= \psi_2 e^{2\pi i \frac{E_2}{h} t} \\ &\dots \dots \dots\end{aligned}$$

and each one corresponds to its appropriate eigen energy value E .

The general solution of (*) is then given by the linear combination :

$$\psi = \sum_n c_n \psi_n e^{2\pi i \nu_n t},$$

where the c_n 's denote the constant amplitudes of the various characteristic vibrations. The squares of the moduli of the c_n 's, the quantities $c_1 \bar{c}_1$, $c_2 \bar{c}_2$, $c_3 \bar{c}_3$, etc., represent the respective probabilities of the different quantum states of the system. The c_n 's must, of course, all be multiplied by a constant factor so that $|c^2| = 1$, that is to say, they must be normalised to give the total probability 1.

The statistical interpretation of Schrödinger's fundamental function ψ_n , and the general function ψ , and finally the interpretation of the coefficients c_n , was given by Born.

This elementary review of Schrödinger's theory and Born's physical interpretation justifies the conclusion that we must abandon any attempt to follow in detail the behaviour of an individual atomic system, and must be content with statistical results governed by probability laws to which groups containing large numbers of similar atomic systems are subject.

The Principle of Causality in Classical Physics and the "Principle of Indeterminacy"

We have just seen that the solution of any problem of atom mechanics involves Schrödinger functions representing the amplitudes of a scalar which is merely a probability, and hence, has only statistical significance. We have here a similar state of affairs to that met with in statistical molecular theories.

It had always been assumed in the past that the phenomena of the physical world were governed by the principle of causality according to which the behaviour of a system is subject to a rigid determinism. The possibility of defining completely by appropriate measurements the initial state of any given system being admitted, it was thought that the study of the physical world was comprehended on the one hand in the search for methods of measurement of ever-increasing accuracy for defining precisely at a given instant the state of a system, and, on the other hand, in the discovery of all the physical laws governing the behaviour of the system. As final result, it should be possible to predict by calculation the state of a system at any time (in the past or future), given the initial condition. The characteristic example of this doctrine was furnished by celestial mechanics.

From the classical standpoint, statistical considerations are not involved, and in the earlier quantum theory by a natural extension of long-established habits of mind it was thought permissible to apply the laws of macroscopic systems to the world of the atoms. The new quantum mechanics has effected a profound change in our ideas on this question, by denying that in studying submicroscopic systems we can ever acquire knowledge of the behaviour of a single atom, electron, etc. In the domain of the atom we must be content with statistical laws.

That a *causal* conception of atomic physics must encounter difficulties of a fundamental kind was foreseen by Heisenberg in 1927 when he showed that, even in an *ideal experiment*, it would be impossible to fix with absolute certainty both position (specified by the co-ordinate x) and the corresponding momentum ($m\dot{x}$), so that a certain *indeterminacy* would necessarily be associated with all measurements of atomic magnitudes.

To illustrate this point we consider an electron revolving in an atomic orbit. If we wish to determine by a single observation the instantaneous position of the electron and its velocity (momentum) we must "illuminate" the electron under a microscope. This will give the position, and at the same time the velocity, of the electron, the latter being obtained by making use of the Doppler effect (variation in λ of the rays absorbed and re-emitted by the electron).

With this observation, however, there will be associated inevitably the Compton effect, that is to say, in the collision between a light quant and the electron, the velocity of the latter will alter. Thus, on the one hand, a more exact determination of the position of the electron is possible by using light of shorter wave-length (γ -rays of wave-length 5 to 50 times smaller than the radius of the hydrogen atom might be employed); on the other hand, the smaller the wave-length λ the greater the accompanying Compton effect, and, hence, the greater the uncertainty in the observation of the velocity. Similarly, to attain high precision in the determination of the velocity by means of the Doppler effect, it is necessary to use radiation of the longest possible wave-length so that the inevitable Compton effect produces little disturbance. But then the exact determination of the position of the electron is impossible.

The product of the uncertainties in the determinations of position and momentum, Δp and Δq , is of the order of magnitude of Planck's constant h ; $\Delta p \times \Delta q \cong h$. This is the "*principle of indeterminacy*," also known as the "uncertainty principle," formulated by Heisenberg.*

In the example on p. 224, dealing with the determination of the position of a light quant by the rapid opening and closing of a shutter in the path of a narrow pencil of monochromatic light, we have already come across a case where there occurs a reciprocal uncertainty. The light quant is deviated (diffraction), but if we use a larger aperture to minimise the deviation and thereby increase the accuracy of the "velocity" determination, the inaccuracy in the *position* co-ordinate is augmented. If, on the other hand, the position is fixed more precisely, the light quant is subject to a larger deviation and the error in the *momentum* increases. It can be verified that again in this case the two errors are such that $\Delta p \times \Delta q = h$, for each of the three co-ordinates.†

* W. Heisenberg, *Zeits. f. Physik*, 43, 1927, p. 172.

† The *principle of indeterminacy* in its numerical form is verified as follows: Let D be the diameter of the aperture, T the time during which it is open. The beam after diffraction can be analysed into plane waves by Fraunhofer's method. In the theory of diffraction it is shown that there are waves of appreciable intensity in the diffracted pencil, at angles with the incident

Electrons exist also in the free state, as in the cathode stream. Is it significant to speak of the trajectory of an electron, in such a case? To decide this question, it is necessary to "illuminate" the electron, but then at every observation determining its position, the electron will receive a new impulse in a chance direction. The zigzag trace obtained by joining up successive observed positions represents the track of the electron only in as much as each observation impresses on the path, a definite perturbation. The concept of continuity of motion must be abandoned.

To conclude, therefore, it is true equally for an electron in an atom, an electron in the cathode stream and a light quant, that we cannot speak of the path traversed, because any attempt to observe this path modifies the motion. We recognise the logical impossibility of considering a phenomenon independently of the means used to study it. It is idle to suppose that laws could be laid down to which phenomena would conform in the absence of all observers.

Viewed from this standpoint, the double aspect—particle—wave—exhibited by radiation and also by matter (Davisson and Germer's experiments), no longer appears as an incomprehensible dualism.

The uncertainty principle obliges us to modify our conception of the principle of causality. If the state of a mechanical system, defined by $2f$ canonically conjugate variables (q_k, p_k) , is represented by a point in the $2f$ -dimensional phase space, we no longer admit

direction of the order of $\frac{\lambda}{D}$, and that in the diffracted spectrum occur frequencies

which differ by $\frac{1}{T}$ from the original frequency. Hence, the uncertainty in the co-ordinate x or in the length of the light "packet" in the direction of propagation, is vT , and the uncertainty in the co-ordinate p_x (the momentum) is $\frac{h\nu}{v} = \frac{h}{vT}$. The product of the two uncertainties is therefore $vT \times \frac{h}{vT} = h$. For the co-ordinate y the uncertainty Δy is D , and for the momentum it is $\Delta p_y = \frac{h\nu}{v} \frac{\lambda}{D}$, $\frac{\lambda}{D}$ being the cosine of p_y with respect to the incident direction. Hence,

$$\Delta y \cdot \Delta p_y = D \cdot \frac{h\nu}{v} \frac{\lambda}{D} = \frac{h\nu}{v} \frac{v}{\nu} = h.$$

Similarly for the third co-ordinate.

that the position of this point can be known exactly at each instant. We can affirm only that it is contained in an element (of the phase space), the volume of which depends on the quantum constant h ; its position within this element is indeterminate. After the system, in obedience to the physical laws to which it is subject, has run its course, the representative point will be in another volume element, and we can only follow these physical laws on the average for an assembly of systems whose representative points are contained in the original volume element.

The physical laws determining the behaviour of systems are thus valid for a group of similar systems, but are incapable of telling us exactly what will happen to an individual system. The idea of determinism is abandoned in its old form, and is now applied only to the probable behaviour of a system.

It is, of course, permissible to believe that behind the statistical laws which control elementary phenomena, there are certain hidden laws to which the individual particles conform, and that, therefore, a concealed causality holds sway which leads to the probability laws revealed by experiment. The fact is, however, that there is not the least experimental evidence for such hidden laws. On the contrary, Planck's constant h appears as a *fundamental limit* in everything we can observe.

The great importance for experimental physicists of the fact that Heisenberg's indeterminacy principle expresses the limit of accuracy of measurement for the conjugate co-ordinates p and q in terms of h , should not escape notice. The presence of the constant h always characterises an experimental phenomenon which *classical* mathematical physics is powerless to explain. Thus the appearance of the constant h in Heisenberg's principle invests the latter with a very profound significance.

Many physicists consider the indeterminacy in quantum mechanics as a temporary phase in the development of science, and look for a return to determinism. Others, however, are convinced that such a return is impossible unless some completely revolutionary discovery of an experimental character is forthcoming which may furnish means—at present lacking—for the detailed investigation of collision phenomena.

***Other Examples of Indeterminacy in the Simultaneous Measurement of Conjugate Variables**

(1) Suppose we wish to determine in an ideal experiment the position of an electron at a given instant. The simplest way is to illuminate the electron and examine it under a microscope, which brings to a focus the light scattered by the electron. The amount of light available will be extremely limited, but that is merely a practical difficulty. Of more importance is the fact that the microscope gives for the image of a point a diffraction figure consisting of a central spot surrounded by diffraction rings. The resolving power of the ordinary microscope is given by Abbe's formula :

$$\Delta x = \frac{\lambda}{2 \sin \alpha} \quad \dots \dots \dots (1)$$

which determines as a function of the wave-length λ and the angular aperture 2α , the minimum distance Δx between two points seen through the microscope as separate. It is clear that Δx determines the maximum precision and the

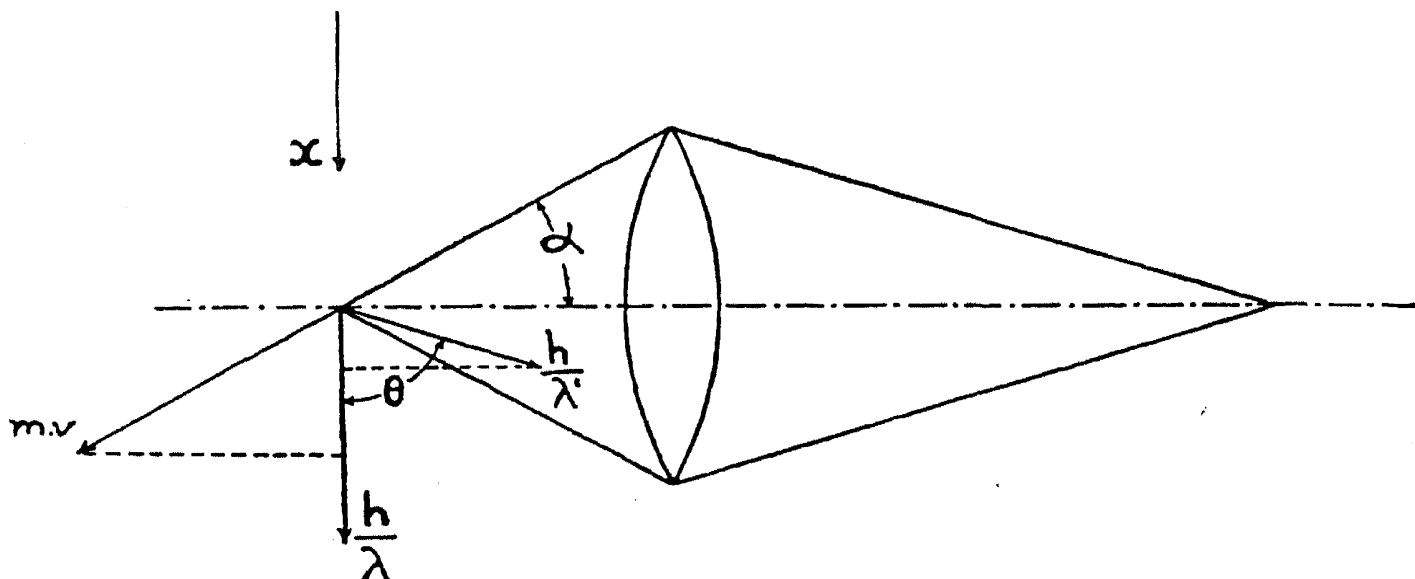


FIG. 73.

smallest error attainable in the measurement of x . It follows from (1), that by making λ sufficiently small x can be measured to any desired degree of accuracy. x may be, for example, a cartesian co-ordinate of the electron in the plane normal to the axis of the microscope.

Thus, using a radiation of very small wave-length we can reduce indefinitely the size of the diffusion disc whose centre determines the electron position. If the electron were stationary it would be possible to illuminate it sufficiently long to obtain the diffraction figure on a sensitive plate (all the aberrations of the ordinary microscope can be considered as eliminated).

Using radiation of high frequency, however, the light quanta will impart appreciable momentum to the electron by Compton effect, so that in determining the position, we alter the velocity of the electron, and by an amount which increases with the accuracy of the determination of position. Moreover, the change in velocity does not take place in a way which can possibly be predetermined, as will be seen.

The theory of the Compton effect indicates that the momentum received by the electron in scattering radiation is calculable by the laws of mechanics, assigning momentum of amount $\frac{h\nu}{c} = \frac{h}{\lambda}$ to the incident light quant, and

momentum of amount $\frac{h}{\lambda^1}$, to the scattered light quant, where λ^1 is a little different from λ .

The momentum p_x acquired by the electron in the direction x of the incident light is :

$$\frac{h}{\lambda} - \frac{h}{\lambda^1} \cos \theta, \quad \text{or approximately} \quad \frac{h}{\lambda} (1 - \cos \theta),$$

where θ is the angle between the directions of the incident and scattered light quants. Now we do not know θ because, in a microscope free from aberrations, whatever the direction of the scattered light quant within the angular aperture of the instrument, the quantum $h\nu^1$ is concentrated at the same point of the focal plane. Thus θ may vary between $(90 - \alpha)$ and $(90 + \alpha)$, and hence the change of momentum p_x may vary between $\frac{h}{\lambda}(1 - \sin \alpha)$ and $\frac{h}{\lambda}(1 + \sin \alpha)$.

It follows that the uncertainty in p_x is given by:

$$\Delta p_x = 2 \frac{h}{\lambda} \sin \alpha$$

and, combining this equation with (1), which gives the uncertainty in x , we have

$$\Delta p_x \Delta x = h.$$

(2) It is desired to determine the component of electron velocity, v_x , at a given instant, making use of the Doppler effect. The electron is illuminated in the direction x and the wave-length change ($\lambda^1 - \lambda$) of the scattered light is determined. The elementary theory shows that :

$$v_x = \frac{c}{2} \frac{\lambda^1 - \lambda}{\lambda}.$$

It is true that in doing this experiment, we alter the velocity because of the Compton effect, but the magnitude of the effect can be calculated and allowed for as a correction to the result (the momentum received by the electron equals $\frac{2h}{\lambda}$, corresponding to an increase of velocity of amount $\frac{2h}{m\lambda}$). We cannot know, however, the precise instant at which this change of velocity occurs, and therefore we cannot know the position of the electron at the conclusion of the measurement.

To measure accurately the wave-length of the scattered light it is necessary to employ a sufficiently long train of waves, or, in other words, to illuminate the electron for a certain length of time. There is no means of determining the precise instant within this interval, when the scattering process occurred.

Using a train of n wave-lengths, the inaccuracy in λ^1 is $\Delta \lambda^1 = \frac{\lambda^1}{n} \simeq \frac{\lambda}{n}$. Hence,

$$\Delta v_x = \frac{c}{2\lambda} \Delta \lambda^1 = \frac{c}{2n}$$

and, therefore,

$$\Delta p_x = m \cdot \Delta v_x = \frac{mc}{2n}.$$

The uncertainty Δx in the conjugate co-ordinate x is obtained from the increase in velocity $\frac{2h}{m\lambda}$, and the period of illumination $\frac{n\lambda}{c}$. In fact Δx is the product of these quantities :

$$\Delta x = n \frac{\lambda}{c} \cdot \frac{2h}{m\lambda} = \frac{2nh}{mc}.$$

Finally, it is seen that $\Delta x \Delta p_x = h$, and again we conclude that the exact position and velocity of an electron cannot be assigned simultaneously.

(3) By Franck and Herz's method we can measure, with a precision to which theoretically there is no upper limit, the energy levels of atoms. Heisenberg points out that it is impossible to measure at the same time the exact instant to which the value of the energy level refers. This is connected with the fact that to know the instant of collision it would be necessary to know the exact position of the colliding electron in a preceding instant. This determination of the position would produce by the Compton effect an indeterminacy in the value of the velocity and hence of the energy. Also in this case, the product of the mean errors ΔE and Δt is of the order of magnitude of h .

It is clear that classical mechanics which employs the concept of simultaneous numerical determination of position and velocity, must contain in itself a contradiction which is not revealed in macroscopic phenomena because, owing to the small value of h , the uncertainties Δx and Δp_x , etc., are relatively insignificant. When atomic phenomena are concerned, however, where x and p_x are themselves very small quantities, these uncertainties are not in any sense negligible, and, in fact, they are responsible for the difficulties which were encountered in applying classical mechanics to atomic phenomena. New postulates had to be introduced to derive the results of experiment, and these already contained implicitly the indeterminacy principle. In this way the quantum constant h made its entry into physics, but a connected development of mechanics taking into account the fundamental indeterminacy of conjugate variables required a complete revision of the methods in use as well as a special mathematical weapon. This work was accomplished by Heisenberg, Born, Jordan and Dirac.

Quantum Mechanics. Heisenberg, Born, Jordan, Dirac *

The new quantum mechanics was founded by Heisenberg in 1925. Almost immediately afterwards Born and Jordan lighted upon the mathematical apparatus suitable for working out Heisenberg's ideas in the *matrix calculus*, a neglected branch of mathematics which as far back as the middle of the past century had been developed in considerable detail by mathematicians, in particular by Hermite. It was in fact the so-called Hermite matrices which came to be used in quantum mechanics. For details of the analysis the reader is referred to the original papers which appeared in the *Zeitschrift für Physik* in 1925.†

Whilst de Broglie and Schrödinger had tried to discover the

* The origin of the new quantum mechanics is to be found in a memoir by Werner Heisenberg, *Zeits. f. Physik*, 33, p. 879, July, 1925. A little later appeared the first applications of the matrix mechanics in the papers of Born and Jordan, *Zeits. f. Physik*, 34, September, 1925, and 35, November, 1925. During the development of the matrix theory, Dirac elaborated a theory based on slightly different principles, but leading to equivalent results.

† Dirac's investigations, in which a special algebra for quantum mechanics is introduced, appeared in the *Proceedings of the Royal Society*, London.

laws of atomic phenomena in the light of classical methods, and to bridge the gap separating the quantum mechanics of atoms from classical physics, Heisenberg—a few months before the appearance of Schrödinger's first paper—started out from the opposite idea. He considered that only a definite renunciation of the deeply-rooted classical representation could lead to a proper understanding of the *régime* obtaining in the atom. He was convinced that, as a fundamental principle in atomic physics, any attempt at *explanation* was pointless and without meaning, and that all magnitudes not susceptible to direct observation should be excluded from atomic theory.

To understand this attitude, we observe that the quantum theory in the study of black body radiation, in the photo-electric effect and also in the Compton effect, introduces into the physical picture nothing of an arbitrary character or which cannot be controlled experimentally. The *number of particles* and their *energy states* are in fact capable of measurement. In the later developments of the theory, however, a new hypothesis makes its entry, the notion of trajectories and electron orbits, an hypothesis which appeared perhaps justifiable to our classically trained minds, but which lay outside the test of experiment. No phenomenon in fact can be shown to depend on the position of an electron in its supposed orbit or on the form of the latter.

The atomic magnitudes directly observable and controllable are the *frequencies* and *intensities* of the spectral lines, and the *energy levels* of atoms, determinable by electron collision experiments.

Thus Heisenberg's theory, avoiding arbitrary interpretations, aims only at confirming and extending the fundamental idea that physical phenomena are essentially discontinuous, and does not pretend to show how the atom is constituted, nor to pronounce on the state of systems during their quantum transitions. This seems to imply a refusal to press into the heart of things, and it is in fact a renunciation. At the same time, the desire to break away from deeply-rooted and essentially "macroscopic" ideas is a sign of strength.

It will be instructive to mention a few of the applications of the theory. The intensities of the spectral lines can be calculated on

the theory, in which they occur simply as the *probabilities* of the quantum transitions. All attempts based on Bohr's quantum theory to interpret quantitatively the helium atom, and to derive its ionisation potential, had failed, but with the aid of quantum mechanics the problem has been solved by G. W. Kellner. Dirac (1926) gave a treatment of the Compton effect in terms of the new mechanics.

In the course of the last few years quantum mechanics has had many other applications. For example, the important formula governing the Zeeman effect, which had been discovered as an empirical result by Landé (see p. 135), was established by Heisenberg and Jordan :

$$g = \frac{1 + j(j+1) + s(s+1) - l(l+1)}{2j(j+1)}.$$

We recall that g is Landé's splitting factor, which occurs in the determination of the separation of the several lines originating from a single line in the Zeeman effect, according to the law :

$$\begin{array}{l} \text{frequency difference between} \\ \text{consecutive lines} \end{array} \quad \Delta\nu = \frac{e}{4\pi m_0 c} mgH.$$

Quantum mechanics has, of course, also raised afresh the problem of the hydrogen spectrum in which the successions of terms are fixed by the total quantum number n , the azimuthal quantum number $l = 0, 1, 2, \dots (n-1)$, and the internal quantum number $j = l \pm \frac{1}{2}$. It is found that, neglecting the relativity correction, the energy is given by $W = -E \frac{h}{n^2}$, which involves only the total quantum number n .

That the energy must vary in proportion to $\frac{1}{n^2}$ is understood from a consideration of the fact that for high values of n , the frequency given by the quantum theory using the relation $\nu = \frac{\Delta W}{h}$ must pass asymptotically into the classical theory result. This is in fact Bohr's correspondence principle.

Now the frequency of revolution of the electron is $\omega = \frac{4\pi^2 m e^4}{n^3 h^3}$,

and this is the classical frequency. The quantum theory frequency on the other hand is :

$$\nu = \frac{R}{n'^2} - \frac{R}{n^2} = (n' - n)R \frac{n + n'}{n^2 n'^2} = R \frac{n + n'}{n^2 n'^2},$$

since $n' - n = 1$ (selection rule).

When n' and n are very large,

$$\nu = R \frac{2}{n^3} = \frac{2\pi^2 m e^4}{h^3} \frac{2}{n^3} = \omega.$$

The terms observed empirically in the fine structure, namely

one term for $n = 1$
 two terms ,, $n = 2$
 three ,, ,, $n = 3$
 four ,, ,, $n = 4$,

were correlated by Goudsmit, Uhlenbeck, Slater (1925) with those predicted from the possible combinations of n l j , assuming that levels with the same n and j , but different l , coincide.

That these terms do effectively coincide is established by the calculations of Heisenberg and Jordan (*Zeits. f. Physik*, vol. 37, 1926), and in the scheme given below the superposed terms are printed close together.

n	l	j
3	2	$\frac{5}{2}$
	2	$\frac{3}{2}$
	1	$\frac{3}{2}$
	1	$\frac{1}{2}$
	0	$\frac{1}{2}$
2	1	$\frac{3}{2}$
	1	$\frac{1}{2}$
	0	$\frac{1}{2}$
1	0	$\frac{1}{2}$

Thus for atoms with a single electron, the subdivision of the energy levels (the fine structure) depends solely on the relativistic term, and Sommerfeld's calculation retains its validity intact, at

least as far as the result is concerned. This will be better understood if we introduce here a few remarks about the Bohr-Sommerfeld-Wilson method.

It was believed until about the year 1924, that the Sommerfeld method contained the fundamental principle of atomic mechanics, the means whereby the energies of the various atoms could be calculated and their spectra predicted. In recent years, however, this quantisation rule, $\int p dq = nh$, has lost much of its value. Its successes, as already pointed out, were the calculation of the spectral series of hydrogen, the explanation of the fine structure by the introduction of relativistic mechanics, and the complete interpretation of the subdivision of spectral lines in the Stark effect. Other *qualitative* achievements stood to the credit of Sommerfeld's method, in connection with the spectra of heavy atoms and X-ray spectra.

But the elegant application to the fine structure of the Balmer lines, rigorously verified by experiment, which appeared to be an extraordinarily strong point in its favour, turned out to be *the result of a chance coincidence*, for while Sommerfeld had investigated only a relativistic origin of the fine structure, the actual structure is also due to the effect of the intrinsic magnetic moment of the electron (spinning electron).

In the last analysis, the Bohr-Sommerfeld method figures, in so far as the results are concerned, as a first approximation to quantum mechanics.

Actually, by the procedure indicated in Chap. II, Sommerfeld obtained the formula (7) of p. 57 for the total energy of the hydrogen atom (or more generally for the case of a single central charge), and this may be written in the form :

$$\text{Total Energy} = -\frac{2\pi^2 m e^2 E^2}{h^2 n^2} - \frac{m \pi^4 e^4 E^4}{c^2 h^4 n^3} \left(\frac{8}{k} - \frac{6}{n} \right).$$

In this formula, E is the nuclear charge, n the total and k the azimuthal quantum number. It has already been explained that as the energy depends also on the azimuthal quantum number k , there will be n closely adjacent energy levels in place of the single

level obtained by neglecting the relativity effect. There are exactly n levels, because k can assume the values 1, 2, 3 . . . n . By combining these energy levels the components of the fine structure are obtained.

Quantum mechanics on the other hand leads to the following results. First of all, if the intrinsic magnetic moment of the electron is not considered, quantum mechanics furnishes for the energy the value :

$$\text{Energy} = -\frac{2\pi^2 m e^2 E^2}{h^2 n^2} - \frac{m \pi^4 E^4 e^4}{c^2 h^4 n^3} \left(\frac{8}{l + \frac{1}{2}} - \frac{6}{n} \right),$$

where l may equal 0, 1, 2 . . . ($n - 1$). The first term in the above expression is the single term of Bohr's original theory.

Taking account now of the spin of the electron in addition to the relativity effect, a further correction is necessary. The energy levels end up by coinciding exactly, each to each, with those calculated by Sommerfeld. This coincidence, as is clear from the brief account just given, is accidental. We have here the explanation of the fact that for many years the Bohr-Sommerfeld theory was successful in explaining, apparently conclusively, the hydrogen fine structure.

In the latest developments of the quantum theory, the impressive evidence for microcosmic planetary systems appears to be irrecoverably lost. How is it then, we may ask, that until a short while ago, physicists emphatically upheld the reality of planetary trajectories and their capacity to explain complicated spectra and the properties of atoms ?

The reason is this. What is real or substantial in atomic models, whether constructed in the old or in the new style, is merely the quantum numbers, the integral numbers $n \ l \ j \ m$ which define the energy of the trajectory, to use a term belonging to the old theory, or the eigen values E , in the language of the new theory. Only the E values play any part in phenomena, or are revealed in observations of spectral lines or in chemical reactions. The quantum numbers can be divested of any signification they appeared to possess in the models based on the old mechanics, but they will retain unaltered their function of determining the energy.

***Reappearance of the Quantum Numbers in the New Mechanics**

The new quantum mechanics, both in Schrödinger's wave formulation and Born's statistical theory, no longer contemplates the orbits imagined by Bohr and Sommerfeld, but it does lead as before to the conclusion that atomic and molecular phenomena are governed by the existence of quantum numbers, each electron in an atom requiring the following four numbers for its specification :

The total quantum number n .

The secondary or azimuthal quantum number l (to which corresponds the moment of momentum $U = \frac{h}{2\pi} \sqrt{l(l+1)}$).

The magnetic quantum number m .

The quantum number s associated with the electron spin.

These four quantum numbers have already been discussed in connection with the motion of an electron in a central field (see the section on the anomalous Zeeman effect, p. 131).

We have seen that to each electron must be ascribed two vectors l_i and s_i , corresponding respectively to the moment of momentum of the *orbital motion* and the moment of the *spin*. The suffix i serves to differentiate the vectors corresponding to different electrons. For atoms containing several electrons the study of the structure of multiplet spectral lines has shown that it is not permissible to treat each electron as though it moved in a central field of force, independently of all the others. It follows that the four quantum numbers per electron referred to above are not all required. The theory of multiplets and atomic magnetism calls in this case for the consideration of the resultant mechanical and magnetic moments due to the orbital motion of the electrons and to the *spin* (intrinsic rotation of the electron).^{*} For each particle within the atom, both the vector l and the vector s must be taken into account.

If these vectors are added (vectorially) for all the electrons in the atom, the total moment of momentum of the atom is obtained and this must also be quantised so that :

$$|j| = \frac{h}{2\pi} \sqrt{j(j+1)}, \text{ where } j \text{ is an integer.}$$

From the spectroscopic data, as we have seen, the vector resultant l of all the l_i 's is similarly quantised, and,

$$|l| = \frac{h}{2\pi} \sqrt{l(l+1)}, \text{ where } l \text{ is an integer.}$$

Finally, the vectors s_i can only be either parallel or anti-parallel, so that for the total quantum number corresponding to the vector s , the sum of the s_i 's, the following possibilities arise :

$$s = \frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \dots$$

for an odd number of electrons,

$$s = 0, 1, 2, 3, \dots$$

for an even number of electrons.

As already mentioned, j results by summation of all the l_i 's and s_i 's, and hence given a value of l , to every s correspond various ways of obtaining, by adding the two vectors l and s , a third quantised vector j . The following is an example.

^{*} Other investigations show that nuclei and protons also possess magnetic moment and spin.

For $l = 2$ and $s = 2$, j can only be 0, 1, 2, 3 or 4. Quintets are formed in this way as there are five levels.

For $l = 1$ and $s = \frac{3}{2}$, $j = \frac{1}{2}, \frac{3}{2}$ or $\frac{5}{2}$, giving triplets.

It is clear that if the vectors j, l, s have respectively the values,

$$\sqrt{j(j+1)} \quad \sqrt{l(l+1)} \quad \sqrt{s(s+1)}$$

Landé's formula results by repeating the brief calculation given on p. 136.

In conclusion, it may be said that experiments on atomic magnetism and spectroscopic analysis reveal a very complex structure in what we have called the magnetic moment of the atom, or in the corresponding mechanical moment, the moment of momentum. These vectors are made up of contributions due to the orbital motion of the electrons in the first place, and, secondly, to the spin properties of electrons and protons. These all combine in accordance with quantum laws.

Some Applications of Wave Mechanics

Schrödinger's theory proves to be a convenient instrument for investigating problems to do with the reciprocal action of light waves and atoms. To this field belong dispersion phenomena, the photoelectric effect, the Auger effect and the Raman effect.

Wave mechanics has also been applied to the problem of the scattering of electrons and atoms (α -particles), in passing through matter. The calculations reproduce the experimental results obtained respectively in the Thomson effect and in Rutherford's experiments described in Vol. I, Chap. IX.

A connected account of these theoretical investigations is given in Sommerfeld's recent book entitled "Wellenmechanischer Ergänzungsband" (Wave Mechanics Supplementary Volume).

Other very important applications have been made, to the theory of homopolar valency* and in the interpretation of the helium spectrum.

Kramers and Heisenberg (*Zeits. f. Physik*, 31, 1925) gave a completely new derivation of the dispersion formula, the exact form of which is thus a wave mechanics result.

As Wentzel† and Beck‡ have shown, Schrödinger's theory provides an explanation of the photoelectric effect, in which Einstein's formula is derived and in which it is shown that the electron emission ought to be a maximum in the direction of the electric vector. Further, it is confirmed that this direction of

* F. London, *Zeits. f. Physik*, 46, p. 455, 1928, and 50, p. 24, 1928.

† G. Wentzel, *Zeits. f. Physik*, 40, 1926, and 41, 1927.

‡ G. Beck, *Zeits. f. Physik*, 41, 1927.

maximum emission is displaced more and more for the short waves.

The theory of the Auger effect was worked out by Wentzel and Fues * and both Gordon † and Wentzel ‡ have dealt with the Compton effect. Many authors, including Heitler, London, Sugiura and Wang, have calculated the energy of the hydrogen molecule § and others have made a similar calculation for the helium atom.

Heisenberg succeeded in explaining ferromagnetism as a phenomenon subject to wave mechanics laws. ||

The Ramsauer effect has also been treated by wave mechanics. We recall that in 1921 Ramsauer discovered a phenomenon which at the time appeared quite inexplicable. If electrons are made to pass through a gas, the deviations which they undergo, as a result of collisions with the gas molecules, depend, as might be expected, on the velocity. Very fast electrons are deviated scarcely at all, while slower electrons are subject to larger deflections. It might be thought then that the magnitude of the deviations should steadily increase with diminution of the electron velocity. Ramsauer observed, however, that just the opposite happens, and when the electron velocity falls below a certain limit further decrease in velocity reduces the deviations.

The Ramsauer effect, or the great transparency of certain gases to slow electrons, is explained by wave mechanics. The effect is observed for the gases helium, argon, neon, etc., which have symmetrical molecules, that is, speaking in terms of the classical theory, molecules with completed outer shells so that the electric field decreases very rapidly with distance. This means that the potential function V in Schrödinger's equation has an appreciable value only at very short distances from the molecule, which therefore behaves, in this respect, as an object of minute dimensions. On the other hand, the wave-length $\lambda = \frac{h}{mv}$,

* *Zeits. f. Physik*, pp. 524 and 726, 1927.

† *Zeits. f. Physik*, 40, p. 117, 1926.

‡ *Zeits. f. Physik*, 43, pp. 1 and 779, 1927.

§ W. Heitler and London, *Zeits. f. Physik*, 44, 1927, and S. C. Wang, *Phys. Review*, 31, 1928.

|| W. Heisenberg, *Zeits. f. Physik*, 49, p. 619, 1928.

corresponding to slow electrons, is very large. Thus the interaction of a molecule of very weak external field, with a slow electron, is precisely analogous to the effect of a small obstacle in a train of waves of large wave-length. The obstacle fails to diffract the waves which pass on practically undisturbed.

Concluding this brief *résumé*, we may say that wave mechanics has shown itself to be the appropriate method for dealing with all the problems of atomic mechanics to which it has been applied. In all cases it has given results in agreement with experiment. From among the many applications of the theory we select four, of which brief accounts will be given in the following sections. These bear on the following topics : (1) *the discovery of the isomerism of hydrogen*; (2) *the theory of radioactivity*; (3) *incoherent scattering (Raman effect)*; (4) *dispersion*.

It may be asked why the more complex problems relating to atoms of three, four or more electrons have not been solved by the aid of these methods. The reason is that the mathematical developments become so complicated that no one has succeeded in reducing them to a manageable form whether using Schrödinger's method or matrix mechanics. Already, in the case of the hydrogen molecule, it is necessary to have recourse to methods of approximation, and even then the calculations become prohibitive.

The Discovery of Parahydrogen. One of the most Brilliant Applications of Wave Mechanics

We recall that the electron possesses a magnetic moment of amount 0.9×10^{-20} c.g.s. units. Recent work has shown that atomic nuclei, or perhaps we should say certain of these, also have a magnetic moment, which is about a thousand times smaller than that of the electron. The existence of this moment is made manifest in various phenomena. It is observed, for example, that the spectral lines of many elements, in particular those of high atomic weight, are made up of closely spaced components which can be distinguished only by the use of spectroscopic method yielding the maximum resolving power. These components correspond to different orientations of the magnetic moment of the nucleus with respect to the rest of the atom.

Another more striking manifestation is to be observed in the spectra of molecules composed of two similar atoms. In many cases it is found that these spectra consist of alternately weak and strong lines. The new mechanics renders possible an explanation of this alternation in intensity which had been observed a long time previously. It appears in fact that the magnetic moments of the two nuclei of the atoms constituting the molecule may be disposed parallel one to the other, or anti-parallel. The strong and weak lines correspond respectively to these two possible orientations of the nuclei. This means that the molecule can exist in one or other of two states having notably different properties. Thus, for example, ordinary hydrogen is a mixture of molecules with the nuclei parallel (orthohydrogen), and molecules with the nuclei antiparallel (parahydrogen). Under ordinary conditions, the numbers of molecules of the two types just mentioned stand in the ratio 3 : 1.

Only at very low temperatures is there a predominance of parahydrogen molecules, which possess a little less energy than the molecules of orthohydrogen. Thus, if hydrogen is kept for several days in the liquid state, the molecules become transformed into parahydrogen and, by evaporation, the latter can be obtained almost pure in the gaseous state. This was accomplished by Bonhoeffer and Eucken in 1929. It should be observed that the specific heat and other physical properties are different from those of ordinary hydrogen.

The co-existence of ortho- and para-molecules is not limited to the case of hydrogen, but holds for all elements with molecules consisting of two nuclei of the same mass and possessing intrinsic *spin* (magnetic moment). The two modifications are in fact observed in the spectra of nitrogen, fluorine, chlorine and iodine, as was shown by Wood and Loomis in 1928.*

The relative intensities of the lines in the band spectra, from which the mixture proportions can be derived, were also measured. These came out to be 2 : 1 for nitrogen, 1 : 1 for iodine.

If the nucleus of the atom forming the molecule did not possess

* *Phys. Rev.* 31, p. 705, 1928.

intrinsic rotation, then according to the theory every alternate line in the molecular spectrum would be missing.

Another very delicate observation has been made in the investigation of band spectra, connected with the existence of isotopes. The phenomenon described above occurs when the two nuclei are completely identical. Small anomalies observed in the band spectra of oxygen in 1929 have led to the conclusion * that not all the nuclei of oxygen are identical. It was detected that out of 10,000 molecules there were eight which contained one atom of mass 16 and one of mass 18, and one molecule which contained one atom of mass 17. These special molecules exhibit, as predicted by the theory, rotational levels characterised by even quantum numbers, and odd rotational levels.

In a similar way the existence of carbon molecules was recognised, in which an atom of mass 12 (the normal value) was united to one of mass 13.

The spectroscopic discovery of the previously unknown oxygen isotopes 18 and 17, and also of the carbon isotope 13, must be regarded as a most interesting achievement of quantum mechanics, for these isotopes are present in too small quantities for their existence to be revealed by Aston's spectrograph.

We shall now examine a little more closely the way in which this discovery was arrived at. The starting point is Schrödinger's theory applied to two similar atoms combined to form a molecule such as hydrogen, H_2 .

The simplest idea we can form of such a molecule is of a "dumb-bell" rotating about an axis perpendicular to the line joining the two spheres. Schrödinger's equation can be applied to this model (see p. 284).

The calculations, which we shall not enter upon here, lead to the result that the eigen functions of the rotator have the simple form :

$$\psi_n = \sin(n\phi),$$

in which ϕ is the angle of rotation and n is the *quantum number*,

* Giaque and Johnston, *Nature*, 123, p. 123, 1929.

which is of course an integer. The eigen energies, or possible energy states of the system, are given by :

$$\epsilon_n = n(n + 1) \frac{h^2}{8\pi^2 I} \quad I = \text{moment of inertia of the molecule.}$$

Finally, the mathematical investigation shows that the eigen values characterised by the quantum number n , number in all $g = 2n + 1$, which means that to the energy level defined by the quantum n , the statistical weight * $g = 2n + 1$ must be attributed.

Clearly a rotation of the "dumb-bell" through 180° , corresponding to a change in the variable ϕ of π radians, effects an interchange in the positions of the two nuclei. There is, however, a substantial difference depending on whether the rotational quantum number is even or odd. In the former case ψ remains completely invariant, in the latter ψ changes its sign. The eigen functions ψ corresponding to n even and n odd are termed respectively symmetric and antisymmetric eigen functions. Thus the complete set of energy levels separates into two systems, one corresponding to the symmetrical function the other to the antisymmetrical function. The probability $a(n, m)$ of a transition between two states depends on their eigen functions in accordance with the formula :

$$a(n, m) = \iint \psi_n \psi_m (q_1 + q_2) dq_1 dq_2,$$

in which the indices n, m refer to the two quantum states, q_1, q_2 are the co-ordinates of the particles and the integral is extended over all possible values of the co-ordinates. It can easily be shown that the probability in question is always zero for a transition between a symmetric and an antisymmetric state. In other words, such transitions cannot occur.† Thus in a molecule formed

* To obtain a clear understanding of the significance of statistical weight, consider, for example, what occurs in the Stark effect. A line of the original spectrum is split up into several components, deriving from a level which in the absence of an electric field is single-valued. If five components are obtained, the statistical weight of the original level is 5.

† The probability must be independent of whether the suffix n is assigned to one nucleus or the other. Also, interchange of the nuclei must leave the value of $a(n, m)$ unchanged. If the two quantum numbers are one even and one odd, $a(n, m)$ will change sign when the nuclei exchange positions. These conditions can only be satisfied if $a(n, m) = 0$.

of two equal atoms, two types of quantum state are possible corresponding to two distinct series of energy levels between which no transition giving rise to radiation can occur. This means that the molecule can exist in two different modifications, one characterised by even rotational quantum numbers, the other by odd. These modifications are termed the *para* and the *ortho* forms respectively. The considerations at present under discussion take no account of the *spin* of the nuclei.

The names ortho and para derive from the fact that observations on the helium spectrum, before the introduction of wave mechanics, had brought to light two completely distinct series of energy levels and associated lines, attributed respectively to *parahelium* and *orthohelium*, lines corresponding to transitions between terms in different series not being observed. (The ortho terms of helium are triplets, the para terms singlets. The new mechanics explains these facts. Triplets are obtained if the two electrons of the helium atom have their magnetic moments parallel, whereas in the para modification the magnetic moments are antiparallel). A feature of this problem of the helium atom is that the ortho terms are three times as numerous as the para terms. In the same way we shall see that for hydrogen the ortho modification has a statistical weight three times that of the para modification.

We return now to the problem of the molecule of an element containing two atoms. If the nucleus possesses *spin*, then in the molecular band spectra the ortho and para terms should appear with alternations in intensity due to the difference in statistical weight of the levels, mentioned above. In the molecule of ortho-hydrogen the nuclear magnets are parallel, for parahydrogen they are antiparallel.

It is important to observe that the evidence for the co-existence of two different modifications is not confined to the spectral characteristics described above. The presence of two modifications is also evidenced in the variation of rotational specific heat with temperature, a phenomenon recognised by Dennison in 1927.*

We recall that the specific heat interpreted as kinetic energy is made up of a contribution due to translational motion and a

* D. M. Dennison, *Roy. Soc. Proc. A.*, 115, p. 483, 1927.

contribution due to rotation. In connection with the latter, experimental work has brought to light certain anomalies, in that at low temperatures (from 75° to 150° absolute) the values obtained at a given temperature show a wide spread. The old quantum theory was successful in explaining in a general way the diminution of C_{rot} with T , but was powerless to deal with an effect of this kind. The difficulty is now cleared up and quantitatively explained by admitting the existence of two kinds of hydrogen.

We have seen that the rotational energy has the value,

$$\epsilon_n = n(n+1) \frac{h^2}{8\pi^2 I}.$$

The average value $\bar{\epsilon}$ is given by statistical mechanics, and is, by definition,

$$\bar{\epsilon} = \frac{\sum g_i \epsilon_i e^{-\epsilon_i/kT}}{\sum g_i e^{-\epsilon_i/kT}}.$$

The numerator represents the sum of the energies, the denominator the number of molecules possessing the various energy values ϵ_i . g_i represents the statistical weight of the state ϵ_i .

To pass from the energy $\bar{\epsilon}$ to the specific heat, we have merely to form the derivative $\frac{d\bar{\epsilon}}{dT}$ and multiply by the number of molecules.

We propose to obtain C_{rot} for parahydrogen and orthohydrogen. Put

$$\frac{1}{kT} = x \quad \text{and} \quad Q = \sum g_i e^{-x\epsilon_i}.$$

Q is the total number of quantum states.

We have,

$$\frac{dQ}{dx} = \sum g_i \epsilon_i e^{-x\epsilon_i} \quad \bar{\epsilon} = \frac{1}{Q} \frac{dQ}{dx} = - \frac{d \log Q}{dx}.$$

As it is usual to refer the specific heat to a gramme molecule, we obtain C_{rot} by multiplying $\bar{\epsilon}$ by Avogadro's number $N = \frac{R}{k}$.

Thus $C = \frac{R}{k} \frac{d\bar{\epsilon}}{dT} = - \frac{R}{k^2 T^2} \frac{d\bar{\epsilon}}{dx}$ since $dT = - kT^2 dx$.

Putting, for brevity, $\frac{h^2x}{8\pi^2I} = \sigma$,

we have $\epsilon_n = n(n+1)\frac{\sigma}{x}$ and noting that $g = 2n+1$

$$Q = \sum (2n+1)e^{-n(n+1)\sigma}$$

$$C = R \frac{1}{k^2T^2} \frac{d^2}{dx^2} (\log Q) \dots \dots \dots (*)$$

These equations contain the desired results. Allowing n to assume all odd integral values, we obtain the rotational specific heat of orthohydrogen, and assigning to n all even integral values, we obtain the corresponding result for parahydrogen.

In other words, we must substitute for Q in (*) the expressions :

$$Q_{\text{para}} = 1 + 5e^{-6\sigma} + 9e^{-20\sigma} + \dots$$

$$Q_{\text{ortho}} = 3e^{-2\sigma} + 7e^{-12\sigma} + 11e^{-30\sigma} + \dots$$

where

$$\sigma = \frac{h^2}{8\pi^2I} \frac{1}{kT}$$

As a practical problem, to determine the rotational specific heats for the two modifications, it is necessary to calculate Q_{para} and Q_{ortho} at a number of temperatures, applying then the equation (*) to obtain C . The value of the moment of inertia to be used in the calculation is given by $I = 4.67 \times 10^{-41}$ gr. cm².

As is usual, at high temperatures the quantisation has no longer any effect, the two modifications yield the same C_{rot} , and the value to which both tend equals 1.98 calories per degree (corresponding to the two rotational degrees of freedom of the dumb-bell).

In Fig. 74, observe, to begin with, the two extreme curves, the upper one referring to 100 per cent. parahydrogen, the lower one referring to 0 per cent. para, *i.e.*, pure orthohydrogen. The outstanding difference between these curves is that whilst the latter descends steadily towards the absolute zero, the curve for 100 per cent. parahydrogen has a maximum at 160° abs. (−113° C.). The curves corresponding to various para-ortho

mixtures are easily obtained from the extreme curves by means of the formula :

$$C = \gamma C_{\text{para}} + (1 - \gamma) C_{\text{ortho}}$$

where γ is the proportion of the para modification present in the mixture. In Fig. 74, which is due to Eucken, the curves for $\gamma = \frac{1}{4}$ and $\gamma = \frac{1}{3}$ are reproduced. These curves represent accurately the experimental data found by Eucken. It is, however, clear that only at higher temperatures can an equilibrium mixture

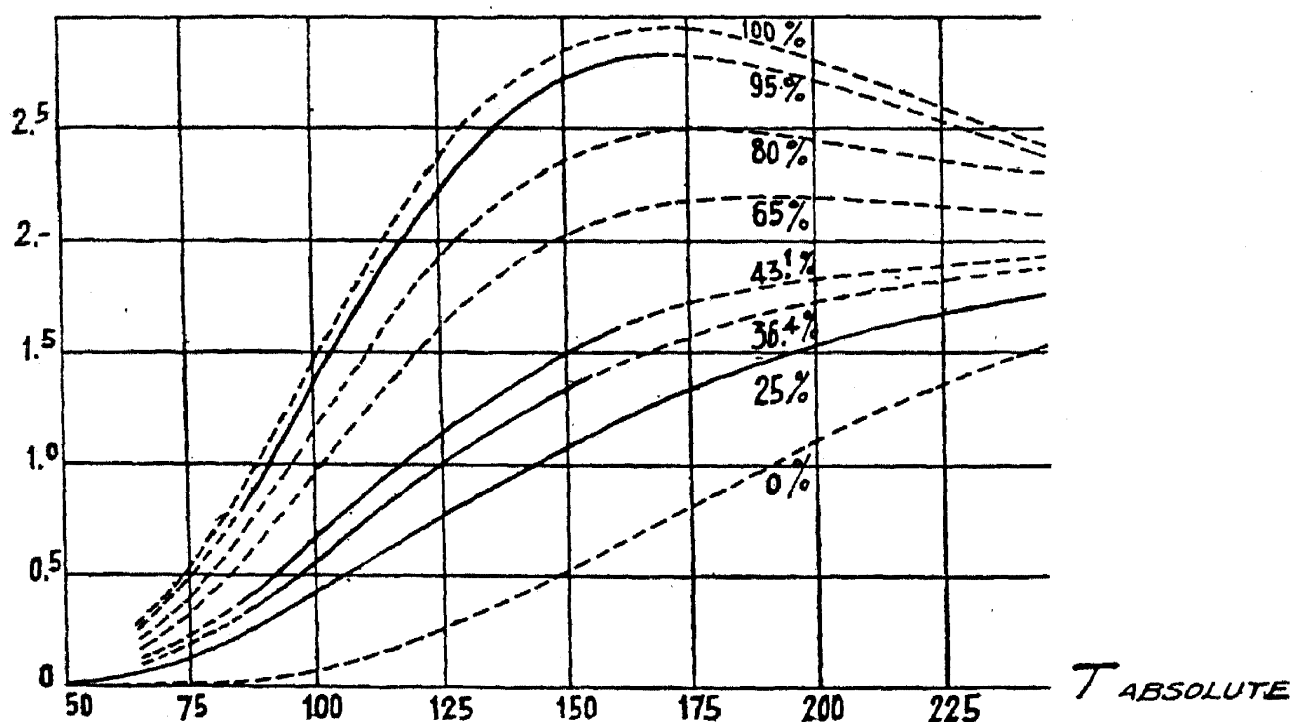


FIG. 74.

contain 75 per cent. of orthohydrogen ($\gamma = \frac{1}{4}$), for at very low temperatures σ has a high value and Q_{para} (frequency, weight) tends to 1 while Q_{ortho} tends to zero.

It was realised that at the lowest temperatures only practically pure parahydrogen would be in equilibrium, and by successive freezings it would be possible to displace the equilibrium ratio in favour of the para modification.

The equilibrium proportions at various temperatures are readily calculated, bearing in mind that the number of molecules possessing the rotational energy ϵ_i is proportional to $3g_i$ for the para, and $1g_i$ for the ortho form, and that the

ratio of the weights of the two modifications in the mixture is given by :

$$\frac{\gamma}{1 - \gamma} = \frac{Q_{\text{para}}}{Q_{\text{ortho}}}$$

The following table gives the results of calculations on these lines.

Temperature.	Percentage of	
	Para.	Ortho.
21.2° Absolute	99.7	0.3
42 " "	86	14
85 " "	48	52
170 " "	25	75

Eucken and Heller in 1929 showed that the variation of specific heat with temperature follows the theoretical curve, also for concentrations different from the normal (25 per cent. parahydrogen). They used high pressures (100–200 atmospheres) and low temperatures (liquid air temperature 70–80° abs.) to obtain, after a week's "exposure," an increase in the proportion of parahydrogen, giving mixtures with 31, 36 and 43 per cent. parahydrogen.*

Other important experiments were made by Bonhöffer and Harteck using charcoal as a catalyst for the formation of parahydrogen.† They allowed the charcoal to absorb gaseous hydrogen at a temperature in the neighbourhood of 21° abs. (temperature of liquefaction), and after twenty minutes the theoretical proportion of 99.7 per cent. parahydrogen had been reached. Successive measurements showed that the proportions of ortho and para hydrogen underwent no further change.

* High pressures were used to accelerate the formation of the equilibrium mixture which otherwise would have been reached only after the lapse of a very long time (of the order of a year).

† Bonhöffer and Harteck, *Zeits. f. Physik. Chemie*, B. 3, p. 113, 1929.

To determine the amount of parahydrogen, Bonhöffer and Harteck did not actually measure the specific heat. They determined instead the thermal conductivity, which is proportional to the specific heat. In a closed vessel containing the hydrogen, and maintained at constant temperature, a wire was hung, its temperature being determined from its electrical resistance. From the current sent through the wire the conductivity could be deduced. Changes in the concentrations of the parahydrogen could thus be followed as changes in the resistance of the wire.

After the preparation of practically pure parahydrogen, its properties could be investigated. Measurements by Bonhöffer and Harteck, and others by Clusius and Heller, have shown that the vapour pressure of the para modification is higher than that of ordinary hydrogen, whilst the solidifying temperature is lower.

Clusius and Heller succeeded in following the variation of rotational heat with temperature in the range 80° to 161° abs. As the uppermost curve in Fig. 74 shows, the rotational heat attains a theoretical maximum value of 2.79 at about 160° abs. Exactly this value was found in the experiments.

In their chemical and electro-chemical behaviour, on the other hand, parahydrogen and normal hydrogen were found to show no difference. Also the heat of solidification was the same for both.

In contrast to parahydrogen, orthohydrogen cannot be obtained in the pure state, because, as the theory shows, there is no possible equilibrium state in which the ortho form is present in an amount exceeding 75 per cent.

Quantum Theory of Radioactivity

In Vol. I, Chap. VIII, it was explained that the phenomena of radioactivity are governed by the laws of probability. It was also pointed out that while the average life of a radioactive atom varies over an enormously wide range, from a millionth of a second (Radium C') to a thousand million years (Uranium), the α -particle is emitted by all the radioactive substances with a

velocity of about 15,000 kilometres per second, which is about 5 per cent. of the velocity of light.*

We recall also that Geiger and Nuttall discovered a relation between the velocity of ejection v of the α -particle—which has a characteristic value for each of the radioactive substances—and the radioactive constant λ .† This relation is expressed by the formula :

$$\log \lambda = A + B \log v \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where B is a universal constant for all the simple radioactive substances and A varies only in passing from one radioactive series to another. If, therefore, $\log v$ is plotted against $\log \lambda$, three straight lines are obtained, one corresponding to each radioactive series (see Vol. I, p. 136).

The explanation of these facts, the interpretation of the mysterious mechanism within the nucleus which causes the α -particle to be expelled, and the calculation of the average life period, have for thirty years engrossed the efforts of physicists. The first successful step in the resolution of these problems was made by G. Gamow, and independently by R. W. Gurney and E. U. Condon,‡ in 1928, by the application of wave mechanics.

After L. de Broglie and Schrödinger had shown that atomic phenomena could be explained by associating with every particle moving in a straight line, a group of waves of wave-length $\lambda = \frac{h}{mv}$, it was recognised that for the α -particles this wave-length would be of the same order of magnitude, as the linear dimensions of the atomic nucleus (10^{-12} to 10^{-13} cm.). In fact, putting $m = 6.6 \times$

* Velocity of the α -particle expelled by	Ra A	.	1.69×10^9 cm./sec.
	Uranium	.	1.40 " "
	Ra C'	.	1.92 " "

The energies corresponding to these velocities are

	Ra A	.	1.22×10^{-5} erg.
	Uranium	.	9.55×10^{-6} "
	Ra C'	.	1.2×10^{-5} "

† The radioactive constant defined by $dn = -n\lambda dt$ is equal to the reciprocal of the average life.

‡ R. W. Gurney and E. U. Condon, *Phys. Rev.*, 33, p. 127, 1929. G. Gamow, *Zeits. f. Physik*, 51, p. 204, 1928, and 52, p. 496, 1928.

10^{-24} gm., and taking v to be of the order 10^9 cm./sec., it follows that:

$$\lambda = \frac{h}{mv} = \frac{6.55 \times 10^{-27}}{6.6 \times 10^{-24} \times 5 \times 10^9} \cong \frac{1}{2} 10^{-12} \text{ cm.}$$

According to ordinary mechanics, if E is the energy of a mass point moving in a field of potential V (a function of position), then the particle is excluded from those regions of space for which $E - V < 0$. If several regions in which $E > V$ are separated by barriers within which $E < V$, there will be many permissible motions of the particle for the given energy value, but each such motion will be confined to one region only, as the barriers effectively prevent transit from one region to another. This was the starting point for the modern theory of the atomic nucleus. At this stage we must explain that whilst ordinary mechanics defines completely the motion of the mass point and contemplates only solutions of probability 1 (the actual motion), or of probability 0 (forbidden motions), wave mechanics defines the motion only in a statistical sense by means of a wave scalar ψ , which is a *function of position and time* and which represents the probability that the particle will be found in a certain place at a certain time.* This result is to be interpreted and used with reference to an assembly of similar elementary systems. The new mechanics applied to the motion of a body in a region delimited by high potential barriers, does not regard the escape of the body as impossible, but leads instead to a certain probability that the event will occur. To sum up, in quantum mechanics the "classical" pronouncement that the particle cannot escape through a barrier where the potential energy exceeds the kinetic energy of the particle, is subject to the following modification: the particle will remain within the barrier for a long time, but the probability of escape increases with time and tends towards unity. As we know, observations on the scattering of α -particles by thin films of gold, silver, copper, etc. (Vol. I, p. 340), have shown that up to a distance from the nucleus of about 10^{-12} cm., Coulomb's law remains valid, so that if Q is the nuclear charge the potential at any external point is given by $\frac{Q}{r}$.

* This probability is actually given by the square of the modulus of ψ .

At exterior points the α -particle is repelled, but in the interior of the nucleus it is attracted and the potential there must be negative. The curve giving the variation of potential with distance rises with steadily increasing slope in approaching the nucleus, and then descends (the dotted line in Fig. 75) when a certain critical distance is reached.

In Gurney and Condon's curve, shown in Fig. 75, the unit along the abscissa is 10^{-12} cm. and the unit along the ordinate equals 10^{-5} erg. The nuclear charge is taken to be $82e$. The three horizontal lines in the figure are drawn at heights of the ordinate corresponding to the kinetic energies of the α -particles ejected by radium C', radium A and uranium. It is seen that in all three cases the potential barrier is high relative to the α -particle energy, although the average life varies from 10^{-8} seconds for RaC', to 3 minutes for RaA and 5×10^9 years for uranium.

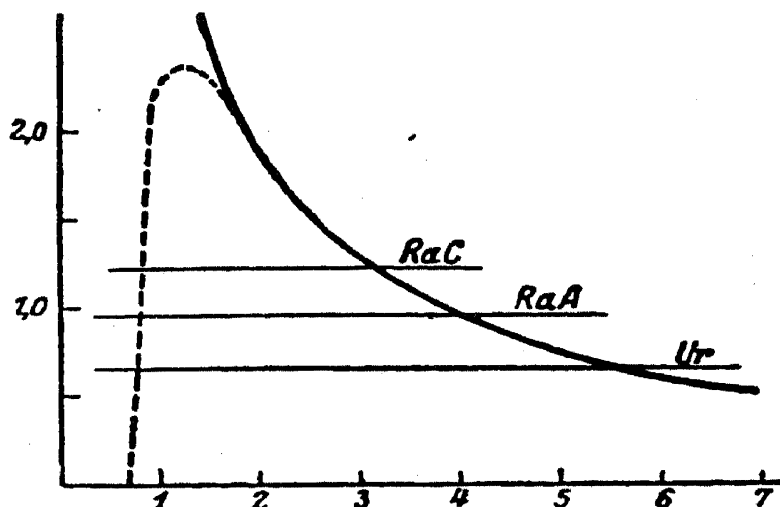


FIG. 75.

By applying wave mechanics, a theoretical reason for the radioactivity of the nucleus, *i.e.*, the expulsion of the α -particle, has been obtained. To give an idea of the very small probability that an α -particle will pass out through the barrier we need only observe that the velocity of the α -particle in the nucleus (which has dimensions of the order 10^{-12} cm.) is about 10^9 cm. per sec. The number of impacts of an α -particle on the barrier in a second will be something of the order $\frac{10^9}{10^{-12}} = 10^{21}$. Since in the case of radium only one out of 7×10^{10} atoms disintegrates in a second, the probability of an α -particle striking the barrier and escaping cannot be more than 10^{-32} , and this is the figure to which the theory should lead. With these brief remarks we pass at once to the result arrived at by the application of wave mechanics.

The radioactive constant of an element, *i.e.*, that fraction of the substance which disintegrates in a second, is obtained in the form,

$$\lambda = \frac{1}{a} \sqrt{\frac{2E}{m}} e^{-\frac{4\pi}{h} \int \sqrt{2m(V-E)} dx}$$

where a is a length of the order of magnitude of the nuclear radius, and m and E have the meanings already noted. The integral is extended through the whole thickness of the "barrier."

We observe that $\frac{1}{a} \cdot \sqrt{\frac{2E}{m}}$ is a quantity which represents the "frequency" of the intranuclear motion, for $\sqrt{\frac{2E}{m}}$ is the velocity,

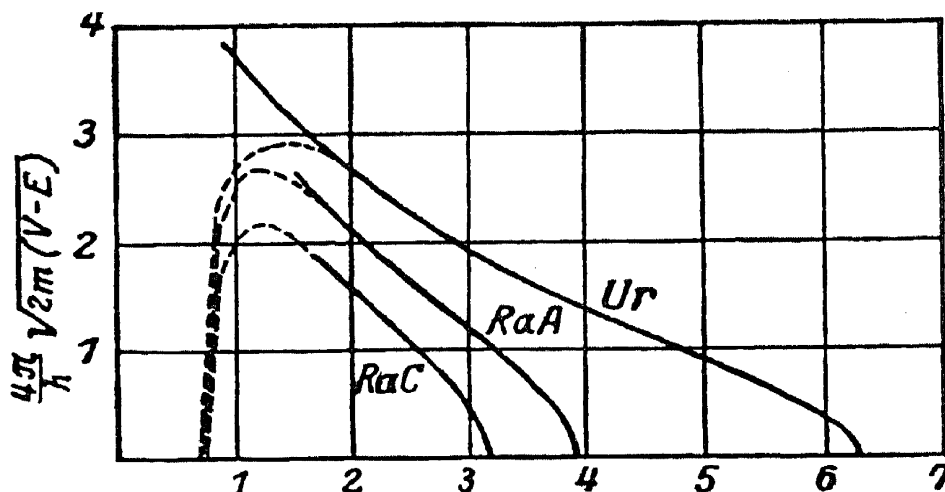


FIG. 76.

and this, when divided by the radius a , gives the number of "gyrations" per second within the nucleus. As noted above,

$\frac{1}{a} \sqrt{\frac{2E}{m}}$ is of the order 10^{21} .

Knowing λ , the period T is obtained from $T = \frac{\log 2}{\lambda}$.

We have now to explain how it is that by varying E , V , and also the nuclear radius, within not very wide limits, the probability is made to vary over such an enormous range of values. In Fig. 76

the quantity $\frac{4\pi}{h} \sqrt{2m(V-E)}$ (in units of 10^{+13} cm.) is plotted against distance from the nucleus (in units of 10^{-12} cm.), for each type of atom. To each unit square of the diagram there correspond

10 units of the product $\frac{4\pi}{h} \sqrt{2m(V - E)} dx$. Inspection of the figure shows immediately that the areas enclosed by the three curves (the area in each case represents $\int dx \frac{4\pi}{h} \sqrt{2m(V - E)}$), vary for the three elements RaC', RaA, Ur., approximately as the numbers 4, $4\frac{1}{2}$, $6\frac{1}{2}$. It follows that the corresponding values of the constant λ will vary as e^{-40} , e^{-45} , e^{-65} .

This then is the reason why, in passing from radium C' to uranium, λ varies in the ratio $1 : 10^{-25}$, whereas the α -particle is expelled from the atom of radium C' with a velocity which exceeds that corresponding to uranium by not more than 40%.

The mere fact that the velocity of the α -particle from RaA is 1.69×10^9 cm. per sec., that is to say, a little greater than 1.4×10^9 cm./sec. (the velocity of the α -particle from uranium) has the result that radium A disintegrates 10^{15} times as rapidly as uranium.

It is easy to see from Fig. 76 that the area enclosed by the curve, which gives the value of λ , is determined principally by the position and shape of the part drawn with a full line and corresponding to the region external to the nucleus. It should therefore be possible to *calculate* λ from a knowledge of this part of the curve only, and this in fact is what Gamow and Gurney and Condon actually did. They determined λ for different elements and obtained results in agreement with the well-known experimental values.

The important expression :

$$\lambda = \frac{1}{a} \sqrt{\frac{2E}{m}} e^{-\frac{4\pi}{h} \int dx \sqrt{2m(V - E)}}$$

can also be written in the form :

$$\log \lambda = -\frac{4\pi}{h} \int dx \sqrt{2m(V - E)} + \log \left(\frac{1}{a} \sqrt{\frac{2E}{m}} \right) \quad (*)$$

and as $\frac{1}{a} \sqrt{\frac{2E}{m}} = \frac{1}{a} v$, we recognise in (*) the celebrated Geiger-Nuttall law, for (*) can be expressed more simply as

$$\log \lambda = A + B \log v.$$

B is a constant which depends only on the units of measurement chosen. A, on the other hand, varies for the three radioactive families. Geiger and Nuttall's diagram indicates that the points referring to members of a given series lie on a straight line, which means to say that the pairs of values (λ, ν) determine a unique value of A for all the elements of one family. As A represents the integral $\int dx \sqrt{2m(V - E)}$, it follows that for the same family the curve in Fig. 76 has the same form.

The fact that α -particles of energy less than 6.5×10^{-6} erg are not observed, is also explained by the theory. It is clear from Fig. 76 that, with decreasing values of E, the curve is raised so that the exponential factor in the expression for λ becomes extraordinarily small. This means that disintegration occurs so slowly that the radioactivity manifested remains below the limit of detection.

Dispersion and Scattering of Light. Smekal-Raman Effect

The phenomena of dispersion and scattering of light were satisfactorily explained in terms of Maxwell's electromagnetic theory. The theory was, however, incomplete in certain points of fundamental importance, connected with the reaction between the molecules of the medium and the radiation. The application of the quantum theory to the dispersion of light, by Ladenburg (1921) and Kramers (1924), and to the scattering of light, by Smekal, Kramers and Heisenberg (1925), led to the complete solution of the difficulties and to the discovery of a new phenomenon, "incoherent scattering," which was predicted by Smekal, and later (1928) discovered, almost at the same time, by Raman and Krishnan in fluids and by Landsberg and Mandelstamm in crystals.

The general problem in the study of the propagation of light in material media is to determine the reactions between the molecules of the medium and the incident light, and to discover what secondary radiations are formed in the process. It is obvious that in general there will be an exchange of energy and momentum between the molecules and the incident radiation.

It is found that the process can be regarded as a kind of collision between the molecule and the incident light quant, in which the molecule can absorb or give up energy by passing from one quantum state to another. In general, therefore, the frequency and direction of emission of the scattered light quant are different from that of the incident light quant. We can imagine that the incident quant is absorbed and another quant emitted by the molecule. The latter is termed the "scattered" light quant. Two cases must be distinguished.

If the quantum state of the molecule does not change during the scattering, the frequency of the scattered radiation practically coincides with that of the incident light, and we have *scattering without change of frequency* or "*coherent*" scattering, as it is also called, for reasons which will be given below. This is the only kind of scattering considered in the classical theory.

In 1923, however, Smekal predicted the existence of another kind of scattering, in which the molecule passes from an energy level E_i to another E_d , so that the energy of the molecule varies by the amount $E_d - E_i$. Let ν_i ν_d be respectively the incident and scattered frequencies.

By the principle of the conservation of energy we must have :

$$E_i + h\nu_i = E_d + h\nu_d,$$

and hence the change in the frequency, $\nu_d - \nu_i$ is obtained as,

$$\nu_d - \nu_i = \frac{1}{h} (E_i - E_d) \quad . \quad . \quad . \quad . \quad . \quad (1)$$

It follows that the frequency change during scattering is necessarily equal to one of the frequencies of the emission spectrum of the molecule (it being possible, moreover, as we shall see, for the corresponding transition to be forbidden by a *selection rule*).

This second kind of scattering is termed *incoherent scattering* or *Smekal-Raman effect*.

It is well known that there is a sharp distinction between the two kinds of scattering. While light scattered without change of frequency can *interfere* with the incident light and give rise to the

phenomenon of *dispersion*,* the light scattered in the Smekal-Raman effect gives rise to no interference phenomena or, more precisely, in the language of the wave theory, the scattered radiations of the individual molecules are incoherent one with another, that is to say, they have varying phase differences and different states of polarisation.

This fundamental distinction can be described most simply by the methods and concepts of the electromagnetic theory. The quantum mechanics and electrodynamics then justify the procedure by assigning a statistical interpretation to the results of the wave theory.

The electromagnetic theory shows that the phenomenon of dispersion, *i.e.*, the variation of the velocity of propagation v of the waves and their index of refraction $n = \frac{c}{v}$, with frequency, can

be explained as a result of the *interference* of the primary incident waves with the *coherent, scattered* waves from the molecules of the medium. The elucidation of this really important and too frequently ignored question is due principally to the work of H. Lorentz (1880–1895), Planck (1902), Oseen, Ewald, and others.

The quantum theory also allows dispersion to be explained as the result of *coherent scattering*.

The picture given by the electromagnetic wave theory is simple. The incident wave induces oscillations in the molecules of the medium, disturbing their stationary state. These molecules acquire an *electric moment* which oscillates with the same frequency, but with a constant retardation of phase with respect to the incident wave. (Just as, for example, an electron attached to an equilibrium position by an elastic force, when placed in an electric field varying according to a sine law, executes forced oscillations having the same frequency as the electric vector of the field, and retarded in phase by an amount depending only on the constants of the system : molecule-field.)

* The phenomena of dispersion we recall, are due to the different refrangibilities of the different frequencies, and to the fact that the ratio $\sin i / \sin r$ is equal to the ratio of the velocities of propagation of the phase in the two media.

We know from the fundamental hypotheses of the electromagnetic theory and from the well-known results obtained with Hertzian waves, that the variable electric moment will generate a spherical electromagnetic wave travelling with the velocity of light, c . The secondary spherical waves with their centres in the individual molecules can interfere with the incident wave. They constitute the wave theory model of *coherent scattering*.

What is observed in dispersion phenomena is the wave resulting from the interference of the primary wave and the waves scattered by the molecules. For this wave the velocity of propagation of the phase of the electric vector comes out to be different from the velocity in vacuo, c .

We obtain in fact,

$$v = \frac{c}{n} \quad \dots \quad (2)$$

with

$$n^2 = 1 + \frac{e^2}{\pi m} \sum_{r,s} N_r \frac{f_{sr}}{\nu_{sr}^2 - \nu^2} \quad \dots \quad (3)$$

where e, m are the charge and mass of the electron, and N_r is the number of molecules per unit volume in the r th state. The ν_{sr} are the frequencies in the spectrum of the molecule and f_{sr} is a constant associated with ν_{sr} and termed the "intensity of the oscillation."

(3), which is termed the "dispersion" formula, is obtained in the same form as here given both in the classical theory and in the quantum theory.*

It follows from what has been said that the velocity of propagation of light waves, constantly under consideration in the wave theory, cannot correspond in any way to the velocity of propagation of a luminous signal (or of a light quant) or of energy.

* The modifications introduced by the quantum theory reduce to the replacement of the notion of oscillating electric moment, by that of *induced transition*, and to the introduction instead of the $f_{s,r}$ of certain constants B which involve the probability of the induced transition $s \rightarrow r$.

$$f_{sr} = h\nu_{sr} B_{sr} \left(\frac{m}{\pi e^2} \right)$$

It may in fact quite well happen that $v > c$, i.e., $n < 1$, as is effectively the case, for X-rays in crystals and for visible light in metals. These velocities, greater than the velocity of light, are in no sense inconsistent with the theory of relativity because the latter affirms only that energy and mass cannot have velocities greater than c and that therefore *signals* cannot be transmitted at higher velocities for the measurement of time.

Besides dispersion, the phenomenon of *coherent scattering* gives rise to the formation of *scattered light*, in the strict sense of the word. Scattering of this kind is observed in turbid, or more generally in heterogeneous, media or media in which the density is subject to "fluctuations" (Tyndall effect, blue of the sky), and has nothing to do with the general phenomenon, common to all substances, which is the Smekal-Raman effect. Moreover, the macroscopic and experimental characteristics of the two kinds of scattering are quite distinct.

It appears that if the molecules of the medium form a perfectly regular space lattice (crystalline) then all the luminous energy scattered by coherent scattering (without change of frequency) is conserved in the *refracted wave* or in the case of double refracting substances, in the two waves refracted by the crystal. In all other directions, the scattered waves and the incident wave cancel out by interference. If, however, there are irregularities in the crystalline structure, if the space lattice is not homogeneous, then the cancellation is not perfect and light is scattered to the sides.

In a similar way, if in a non-crystalline homogeneous medium the molecules are distributed in "complete disorder" (which can be suitably defined) then the coherent scattering gives rise only to a refracted wave in accordance with the ordinary laws.

It remains to consider *incoherent scattering* or the Raman effect. The effect can be observed with the following arrangement. The mercury arc gives an emission spectrum containing a group of very narrow and intense lines (e.g., $\lambda = 2,537, 3,130, 3,650, 4,047, 4,358$ and $5,461$ Ångström units). A system of lenses enables the light from the arc to be directed on to a scattering substance, a

vapour, a liquid or a solid, such as, for example, benzene vapour, NH_3 , N_2 , O_2 , water, ice, crystals, glass. The light is scattered in all directions. Collecting the light in a spectrograph, the spectrum of the scattered radiation is obtained. If the incident light contains one monochromatic line only, the spectrum is found to be made up of a very intense line corresponding to coherent scattering of the Rayleigh type (scattering due to fluctuations of density) and of a group of extremely weak lines disposed on either side of the principal line. The weakness of these satellite lines or Raman lines is such that frequently exposure times of hundreds of hours are necessary to obtain well-defined images.

The phenomenon at first sight resembles the well-known *fluorescence* effect.* In this case also the substance illuminated emits, in addition to the incident frequency, other lines of different frequency, but we note particularly, *always less* than the incident frequency (Stokes' rule). It is clear then that there is a fundamental difference between the two phenomena. In fluorescence the molecule absorbs, partially or totally, the incident light quant and passes from the normal quantum state 1, to a higher, say, the n th state. Subsequently the molecule, in returning to another of its quantum states, for example the m th state with energy E_m less than E_n , emits a line of frequency

$\nu_{nm} = \frac{1}{h} (E_n - E_m)$. It is clear that Stokes' rule holds, for ν_{nm} is less than ν_{n1} , and this is less than the frequency ν of the incident light.

The fluorescence frequencies are actual lines of the spectrum of the molecule. In the Smekal-Raman effect, on the other hand,

* A few words about the phenomenon of fluorescence may be useful. An atom can be excited either by the addition of mechanical energy or by the action of radiation, and the return of the atom to its normal state may occur with or without the emission of radiation. When the excitation is brought about by incident radiation and the return to the normal state is accompanied by emission, we have the phenomenon of fluorescence. Actually the light scattered may be the same as that incident or on account of the partial restitution of the energy, various discontinuous frequencies may be emitted, never higher than the incident frequency. These discrete frequencies represent, as is well known, the energy levels of the atom or molecule, and the emitted quantum $h\nu^1$ is equal to that absorbed $h\nu$ less the difference $E_1 - E_2$ between the two energy levels concerned in the process. In the special case $h\nu = h\nu^1$ we speak of *resonance*.

the "combination" frequencies are from what we have said equal to $\nu \pm \nu_i$, and hence their values vary continuously with, and depend essentially on, ν . Only the *differences* between the frequencies of the Raman lines and the exciting frequency are characteristic of the molecule.

It has been definitely established by experiment that :

(a) Using a single exciting line, the spectrum obtained is symmetrical with respect to the primary radiation. The lines towards the red are more intense than those towards the violet. By analogy with the case of fluorescence, lines of lower frequency than the primary line are termed Stokes' lines, those of higher frequency anti-Stokes' lines.

(b) If the incident radiation is changed the number and positions of the lines obtained remain the same, and only the ratios of the intensities of the modified lines to the intensity of the primary line alter.

(c) The differences between the frequencies of the new lines, and the frequency of the primary line, are identical with the characteristic frequencies of the molecules of the scattering substance, and belong therefore to the infra-red. In crystals the differences coincide with the "residual rays," that is, the rays which are reflected most strongly. These frequencies correspond to particular oscillations of the ions composing the crystal lattice.

The following table gives a numerical example of the Raman effect obtained with carbon tetrachloride, using rays emitted by a mercury vapour lamp.

Incident Line.	Scattered Light Spectrum.	Frequency Difference.	
$\lambda = 4,047 \text{ \AA}$	4,098.3	311 Ångströms	(a)
	4,127.7	455 ,,	(b)
	4,174.4	755 ,,	(c)
$\lambda = 4,358 \text{ ,,}$	4,299.4	314 ,,	(a)
	4,419.0	314 ,,	(a)
	4,272.6	460 ,,	(b)
	4,447.0	458 ,,	(b)
	4,507.3	758 ,,	(c)

It is very convenient to regard the Smekal-Raman effect as a kind of collision between a light quant and a molecule, in which the quant $h\nu$ gains or loses the difference $E_d - E_i$ and is converted into a new quant of frequency :

$$\nu_d = \frac{h\nu_i \pm (E_i - E_d)}{h} = \nu_i \pm \nu_{id}.$$

In this way the effect in question is fitted into the same picture as the other phenomena already examined.

Turning now to the question of line intensities, we know that the molecules of a material medium are distributed among a series of quantum states of energies $E_1, E_2, E_3 \dots$. If we assume the statistical distribution to be in accordance with Boltzmann's law then the number of molecules in the typical state E_i is given by :

$$n_i = NCg_i e^{-E_i/kT} \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where C is a constant, N is the total number of molecules, g_i is the statistical weight of the state in question and k is Boltzmann's constant.

It is clear from this expression, why the lines displaced towards the red are more intense than the corresponding lines on the other side of the primary ray. The former correspond to molecules which lose in energy value, and these molecules are more numerous than those of higher energy. In fact, the smaller the value of E_i the larger $e^{-E_i/kT}$. Thus the statistical equilibrium results in the anti-Stokes' being less frequent than the Stokes' transitions.

The question of intensity is of fundamental importance in *incoherent scattering*. Quantum mechanics and electrodynamics lead to the following expression for the intensity of a scattered line :

$$I_d = \left[F \sum_K a_{iK} a_{Kd} \left\{ \cos 2\pi t (\nu_i \pm \nu_{id}) \times \left(\frac{c_i}{\nu_i - \nu_{iK}} + \frac{c_i}{\nu_i + \nu_{iK}} \right) \right\} \right]^2 \quad . \quad . \quad (5)$$

In this formula F is the amplitude of the primary radiation, c_i

is a constant proportional to the number of molecules present in the i th state. a_{iK} a_{dK} are numbers which determine the probabilities of the spontaneous transitions from the state K to the states i and d .

The law (5) was first obtained by Kramers and Heisenberg (1925) in their theory of dispersion, and it can now be established from a more correct standpoint by the use of quantum mechanics methods. The singular feature about this formula is that it does not contain the probability of the transition $i \rightarrow d$. For a Raman line $\nu_i \pm \nu_{id}$ to have a *non-vanishing* intensity, it is sufficient for the two states i and d to be capable of combining with a third state K . The transition $i \rightarrow d$ may be forbidden. It follows that, although every Raman line corresponds to a definite line in the spectrum of the molecule, the intensities in the two cases may be altogether different.

This state of affairs was first realised by A. Carrelli (1928), closely followed by other authors. A brilliant application was made by Rasetti, studying the Raman effect for the diatomic molecules O_2 , N_2 (band spectra). By very delicate measurements he succeeded in verifying the selection rule which is derived from (5), and in this way confirmed the validity of the formula. The relative intensities of the individual lines were also verified experimentally.

The importance of the Raman effect in the investigation of the properties of molecules is daily increasing. It enables valuable conclusions to be drawn as to the structure of molecules (*e.g.*, it enables the moment of inertia of diatomic molecules of the type N_2 to be calculated with respect to a "transverse" axis), and, in particular, leads to the derivation of the rules according to which singlet spectral terms combine.

Faraday Effect and the Anomalous Magnetic Rotation of the Plane of Polarisation of Light

Among the numerous magneto- and electro-optical effects, the first to be discovered was the Faraday effect (1845). This concerns a *general property* of isotropic substance whereby these acquire in a magnetic field optical properties characteristic of certain crystalline media. Faraday was able to establish that solids and liquids placed in a magnetic field produce a rotation of the plane of polarisation of light if the latter is propagated in the direction

of the lines of magnetic force. This rotation is similar in many respects to the well-known rotation observed with sugar solutions, and which is utilised in saccharimetry, or to that produced by quartz crystals cut normally to the optic axis.

The sense of the rotation depends upon the medium under examination and does not depend on the direction of propagation of the light, so long as this lies parallel to the lines of magnetic force. For diamagnetic substances the rotation occurs in the same sense as the electric currents giving rise to the magnetic field (these currents may be, for example, the currents in a solenoidal coil of an electromagnet, or the molecular currents of Ampère). For paramagnetic substances the rotation is in the opposite sense. The angle of rotation α is proportional to the field H and to the length l of the path of the ray in the field :

$$\alpha = K l H \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

The constant of proportionality K is termed Verdet's constant. The theory of the phenomenon was given after the creation of the electromagnetic theory of light, or rather, the Faraday effect along with the Zeeman effect and the electro-optical effects formed the principal basis upon which the electromagnetic theory was constructed. Fundamental investigations, both experimental and theoretical, of these phenomena have led to the discovery of certain other important effects. Among these, of particular note is *anomalous magnetic rotation* discovered by Corbino and Macaluso. Corbino (1898) observed that the law (1) becomes more complicated when the observations are made with radiations of frequency ν close to the frequency ν_0 of an absorption line of the substance which placed in the magnetic field rotates the plane of polarisation. Passing the light from the sun through a nicol and then through a sodium flame, in a direction parallel to the magnetic field, Corbino and Macaluso observed anomalous rotation of the plane of polarisation for wave-lengths close to the characteristic sodium line (5,890 Å.). In this way rotations of 270° were obtained, whereas for other wave-lengths formula (1) gave a rotation of not more than a few degrees.

The phenomenon was also studied by Righi and theoretically by Voigt. His explanation is analogous to the explanation of anomalous dispersion. It is found that the Corbino-Macaluso effect is closely related to the Zeeman effect of the same substances, and obeys a law of the type :

$$\alpha = \nu^2 l H \sum_K \frac{a_K}{(\nu_K^2 - \nu^2)^2} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Here the ν_K 's are the characteristic frequencies in the absorption spectrum of the substance, ν is the frequency of the light employed and the a_K 's are the constants which also appear in the theory of light dispersion.

This formula takes the place of formula (1) and defines the law of variation of Verdet's constant K , with change of the frequency ν of the incident light. There is an obvious analogy between (2) and the Heisenberg-Kramer's dispersion formula discussed on p. 341.

The quantum theory of the Faraday effect has been given by Born and Jordan. The molecules of a substance are orientated at random in the absence of an external magnetic field. We have in that case "degeneracy of the spatial orientation" (in German, "Richtungsentartung").

On the other hand, in a magnetic field *spatial quantisation* supervenes, determining a regular orientation of the magnetic moments of the atoms and electrons. The Faraday effect is a consequence of this. The Corbino-Macaluso effect depends on resonance between the incident radiation and the molecules of the substance under examination.

It is worthy of note that the theoretical explanation allows us to deduce from measurements of Verdet's constant for diamagnetic substances, the ratio $\frac{e}{m}$ for the electron (Ladenburg). For diamagnetic substances the constant is sensibly independent of temperature, whereas for the "paramagnetic" Faraday effect, the Verdet constant is inversely proportional to the absolute temperature, as is the case for the Curie constant. The paramagnetic effect is observed in crystals of salts of the rare earths (G. Becquerel and de Haas) and in certain gases (caesium vapour).

The quantum explanation of the two phenomena bearing the names of Faraday and Corbino-Macaluso, is obtained without difficulty by considering the effect produced by a constant magnetic field on the dispersion of the light.

The theory of perturbations leads to the conclusion that the electrical moment of a molecule executes a forced oscillation under the influence of the incident electromagnetic wave. The amplitude of this oscillation depends on the frequency and state of polarisation of the incident light. Born and Jordan show that, resolving the incident light into two circularly polarised components (by the known method of Fresnel), these two components are propagated in the magnetic field with different velocities. It follows that on emerging from the medium these two components recombine with a phase difference and in consequence give rise to the phenomenon of rotation of the plane of polarisation.

An analogous explanation can be given for the Kerr electro-optical effect. An isotropic substance (as, for example, carbon disulphide or nitrobenzene) placed in an electric field, rotates and modifies the orbits of the electrons in the atoms. As a first consequence we have the Stark effect, but, in addition, the law of propagation of the light in the medium, is modified by the electric field. The medium, initially homogeneous, loses this property in the electric field, and the components of the light vector (parallel and perpendicular to the field) are propagated with different velocities. This results in double refraction. Light linearly polarised and propagated at right angles to the field direction emerges elliptically polarised. The phenomenon is made use of, as is well known, in the *Kerr cell*, which serves as a means for modulating luminous intensity by a variable electric field.

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CHAPTER IX

THE NEW STATISTICS. APPLICATIONS

Entropy and Probability

To give a clear idea of Fermi's theory, it is necessary to begin with certain preliminary notions of the entropy and probability of a given state of a gas. We refer back first of all to Vol. I, Chap. IV, and the ideas of Boltzmann. In the kinetic theory of gases, a great number of independent parameters are necessary to define completely the state of a gas. The co-ordinates and velocity components of each molecule must be assigned. As a complete knowledge of the motion of the molecules is unattainable, recourse is had to the calculus of probabilities and to statistical mechanics. In this way we arrive at a knowledge of certain magnitudes (temperature, kinetic energy, pressure) which figure in laws subject to practical test.

It is then clear that a particular state of a gaseous mass, determined from the thermodynamic standpoint by fixing say the temperature and the pressure, can be realised by many different combinations of the molecular parameters, which in fact continually "evolve" with time, although still determining the same macroscopic state of the gas. The greater the number of such *complexions* corresponding to a given state of a gas, the more probable the state. The number of complexions can be taken as a measure of the probability.

The relation between this probability W and the entropy S of a gas, established by Boltzmann, takes the form,

$$S = k \log W \dots \dots \dots (1)$$

The significance of the constant k was discussed in Vol. I, Chap. IV. It has the value $\frac{R}{N}$, where $R = 8.32 \times 10^7$ is the perfect gas constant, and

$N = 60.6 \times 10^{22}$ is Avogadro's number. It follows that $k = \frac{R}{N} = 13.7 \times 10^{-17}$ c.g.s. units.

Before giving the proof of this important law, it may be useful to note that the expression *entropy* $= k \log W$ was obtained by neglecting an additive constant. This is permissible because entropy is not definable in the absolute sense, but only with reference to a particular initial state. Only *differences* of entropy can be measured, as in the analogous case of the gravitational potential energy of a body, which is referred to an arbitrary level. The variations only are known, never the absolute value.

We consider for the sake of simplicity a perfect monatomic gas.* The velocity components $u v w$ of each molecule are represented by a velocity point.

* The energy then consists solely of the translational kinetic energy of the molecules, rotational and intermolecular energy being excluded.

From among n molecules contained in one cubic centimetre let there be n_1 which have their velocity points in an elementary parallelopiped at the point $u v w$ of volume $d\tau = du dv dw$.

By Maxwell's law :

$$n_1 = n \cdot f \cdot d\tau = na\epsilon^{-hmc^2} d\tau \quad \dots \quad (2)$$

where

$$a = \sqrt{\frac{h^3 m^3}{\pi^3}}.$$

The different elements of volume, assumed equal, will contain $n_1, n_2, n_3 \dots$ velocity points, and we shall have

$$n_1 + n_2 + n_3 + \dots = n$$

Maxwell's law can also be expressed in the following form :

$$\rho = \frac{n m^{\frac{3}{2}}}{(2\pi kT)^{\frac{3}{2}}} e^{-\frac{m(u^2+v^2+w^2)}{2kT}} \quad \dots \quad (\alpha)$$

where ρ is the density of the representative points in velocity space, k is Boltzmann's constant, and T is the temperature of the gas. The equivalence with (1) is obvious remembering that $h = \frac{1}{2kT}$.

Suppose one of the possible distributions of the representative points, actually realised. By permuting among themselves the n_1 velocity points contained in the first volume element, $n_1!$ complexions are obtained which are indistinguishable one from another and from the original distribution, because they correspond to the same macroscopic state of the gas. Similarly by permuting the n_2 velocity points in the second element, $n_2!$ equivalent complexions are obtained, and so on. In all there will be $n_1! \times n_2! \times n_3! \times \dots$ equivalent complexions. If, on the other hand, all the velocity points are permuted in all possible ways, $n!$ distributions are obtained. These contain, however, many equivalent dispositions, and we are interested in those which remain distinct one from another, for defining the macroscopic state of the gas.

The number of distinguishable complexions is given by :

$$W = \frac{n!}{n_1! \times n_2! \times n_3! \dots} \quad \dots \quad (3)$$

This result can be transformed into a more convenient form by using a famous formula due to Stirling, which is valid for large numbers. Stirling's formula states that the logarithm of $A!$ is given with high accuracy by :

$$\log A! = A \log A - A$$

when A is very large.

In the present case :

$$\log W = -[n_1 \log n_1 + n_2 \log n_2 + n_3 \log n_3 + \dots] \quad \dots \quad (4)$$

A constant term has been dropped as it does not contribute to the final result. This will be better understood in the sequel.

Noting that :

$$n_1 = nae^{-hmc^2} d\tau$$

we obtain :

$$\log W = -n \log (na) + hmn \int c^2 a \epsilon^{-hmc^2} d\tau$$

where the integral is clearly equal to C^2 the mean square velocity of the

particles. In fact the integral is merely the mathematical definition of this quantity (Vol. I, see p. 57). Thus

$$\log W = -n \log (na) + hmnC^2 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

or, since

$$C^2 = \frac{3}{2hm}$$

$$\begin{aligned} \log W &= -n \log (na) + \frac{3}{2}n \\ &= \frac{N}{V} \log (T^{3/2}V) + G/V \quad . \quad . \quad . \quad . \quad . \quad (6) \end{aligned}$$

where G is a constant.

This result refers to a unit volume containing n molecules. For the molecular volume V therefore,

$$\log W = N \log (T^{3/2}V) \quad . \quad . \quad . \quad . \quad . \quad (7)$$

where again a constant has been abandoned.

To relate this result with the entropy and arrive at the end in view, it now only remains to calculate directly the entropy of a perfect monatomic gas as a function of the temperature and the molecular volume, which we proceed to do.

By the definition, change of entropy is given by dQ/T . The heat energy dQ imparted to the gas is employed in doing external work $p dV$ and in raising the temperature by the amount dT .

$$\text{Thus} \quad dQ = C_v dT + p dV.$$

Since $pV = RT$, this can be transformed to give

$$\begin{aligned} dQ &= C_v dT + p d\left(\frac{RT}{p}\right) = C_v dT + pR d\left(\frac{T}{p}\right) \\ &= C_v dT + R \left(dT - dp \frac{T}{p}\right). \end{aligned}$$

The differential of the entropy is therefore :

$$dS = \frac{dQ}{T} = C_v \frac{dT}{T} + R \left(\frac{dT}{T} - \frac{dp}{p}\right).$$

This is easily seen to be the total differential of the function,*

$$S = C_v \log T - R \log V = R \log (T^{3/2}V) \quad . \quad . \quad . \quad . \quad (8)$$

Comparing with (7) above, it follows that :

$$\text{Entropy} \quad S = \frac{R}{N} \log W$$

which is Boltzmann's result, which we set out to prove. The constant k in the expression $S = k \log W$ is seen to have, as stated, the value $\frac{R}{N} = 13.7 \times 10^{-17}$.

Up to this point the statistical calculations have been based on Boltzmann's work. We shall now turn to the consideration of Fermi's ideas.

* If desired, it may also be written,

$$\begin{aligned} S &= R \left(\frac{3}{2} \log T + \log V\right) = R \left(\frac{3}{2} \log T + \log T - \log p\right) \\ &= R \left(\frac{5}{2} \log T - \log p\right) \end{aligned}$$

and for a single molecule,

$$S = \frac{R}{N} \left(\frac{5}{2} \log T - \log p\right).$$

Entropy of the Monatomic Perfect Gas

In the kinetic theory of gases we examined the law of distribution of velocities, determined the average kinetic energy of the molecules and arrived at the values of the specific heats, using the notion of degrees of freedom. As a sequel to this coherent scheme of ideas we have just determined the probability of a given state of a gas, and have related this probability to the entropy calculated directly from thermodynamics. In these calculations certain additive constants were left out of account, for the reason that entropy is not definable in absolute value but only as a difference measured from an arbitrary initial state, so that additive terms have no importance. In this way we have arrived at the expression $S = k \log W$ containing no additive constants.

The quantum theory has not entered into consideration up to now, but bearing in mind the perfect explanation of the variations of the specific heats obtained by quantisation of the elementary oscillators whose energy represents the heat possessed by a body, we soon convince ourselves of the necessity for the quantisation of the molecular motions, the admission of the principle that the translational energy of a molecule can assume only certain discrete values, which must involve Planck's constant.

The entropy, which is closely connected with the kinetic energy of molecular motion, will then also necessarily contain h , the quantum of action. In the case of the specific heats, the quantum discontinuity gave rise to noticeable effects only at low temperatures. Here also we may expect the divergence between the entropy calculated by the classical method, and according to modern views, to be appreciable only at low temperatures, or at high pressures, or, in one word, for condensed states of the gas (*degeneration*).

In an exactly similar way, in Planck's theory of the distribution of energy in the spectrum of a black body, Planck's distribution differs from that arrived at without use of *quantum* ideas, only when low temperatures are approached.

To simplify matters, we reduce the molecular energy to kinetic energy of translation only, by considering monatomic molecules which, as already pointed out, cannot possess internal energy.

With these preliminary remarks we proceed to the calculation of the absolute value of the entropy before introducing Fermi's theory.

Consider a perfect gas consisting of n point molecules enclosed in the volume v . Let it be desired to calculate the absolute value of the entropy. Divide the volume v into a large number of parallelopiped cells in such a way that in each cell there is one molecule only, and let a, b, c be the sides of one such cell.

A calculation, due to Brody (1921), shows that the possible quantum energies of a molecule for motion parallel to a , are given by :

$$W = \frac{h^2 i^2}{8ma^2}.*$$

i is an arbitrary integer, m the mass of the molecule, h Planck's constant.

The probability of the molecule being in the energy state W is given as we know by $e^{-W/kT}$, and the corresponding entropy by

* To understand how this expression for W is obtained, consider a parallel-sided cell of sides a, b, c , the walls of which are perfectly elastic. Suppose the molecule within the cell moves with velocity components v_a, v_b, v_c parallel to the three principal directions. These velocities never diminish in absolute magnitude, but are continually *reflected* when the molecule strikes the walls of the cell. In these circumstances the molecule becomes an harmonic oscillator.

Sommerfeld's condition $\int p dq = nh$ in this case takes the form :

$$2 \int_0^a m v_x dx = i_1 h$$

and two similar equations for the b and c directions. Here i_1 , etc., represent integers.

As $m v_x$ is constant it follows that

$$2 \int_0^a m v_x dx = 2 m v_x a = i_1 h, \text{ etc.}$$

Finally, the total kinetic energy of the molecule is given by :

$$\begin{aligned} W &= \frac{1}{2} m (v_x^2 + v_y^2 + v_z^2) \\ &= \frac{h^2}{8m} \left(\frac{i_1^2}{a^2} + \frac{i_2^2}{b^2} + \frac{i_3^2}{c^2} \right) \end{aligned}$$

and for the first of the three motions, the energy will be $\frac{h^2 i^2}{8ma^2}$ the result given by Brody.

the logarithm of this expression. To obtain the total probability it is necessary to vary i from zero to infinity by steps of one unit, and then to sum with respect to i , preparatory to taking the logarithm.

We now have enough data to calculate the entropy. The increment in the kinetic energy of a molecule is given by $\frac{3}{2} \frac{R}{N} dT = \frac{3}{2} k dT$, and for a gramme-molecule by $\frac{3}{2} R dT = C_v dT$.

The corresponding increase in the relative entropy is $\frac{3}{2} \frac{R}{N} \frac{dT}{T}$, which

is the differential of $\frac{3}{2} \frac{R}{N} \log T$. The latter, however, cannot be the true entropy, because, owing to the step-wise variation of the energy referred to above, it is necessary to add to the quota determined from the continuous rise of temperature a contribution corresponding to the sum of the discontinuities. In short, a not too difficult calculation leads to the following expression for the entropy of a molecule for one *degree of freedom* :

$$\frac{k}{2} \log T + k \log \left[\frac{a}{h} \sqrt{2\pi m k e} \right],$$

(e = base of natural logarithms).

For three degrees of freedom, noting that in taking the sum the expression $\log a \cdot b \cdot c = \log v_c$ (v_c = volume of one cell) makes its appearance, the entropy will be :

Entropy of a molecule

$$\frac{3}{2} k \log T + k \log \left[v_c \frac{\sqrt{(2\pi m k e)^3}}{h^3} \right].$$

For n molecules the entropy is n times this value.

The question now is to find the effective entropy of the gas. Up to the present it has been supposed that each cell contains only one molecule. The probability P that this shall occur, or better, the number of dispositions of the molecules for which this

condition is satisfied, is given by $P = \frac{n!}{n^n}$, that is, the number of ways $n!$ of distributing n objects in n cells, each cell to contain one

object, divided by the number of ways n^n in which the distribution can be effected when no restriction is placed on the way the objects are grouped among the different cells.

Thus, to obtain the true entropy of the n molecules forming the gaseous mass, it is necessary to subtract from the result arrived at above, the quantity :

$$k \log \frac{n!}{n^n} = k \log e^{-n}.*$$

Using this relation and the formula appropriate to the perfect gas, $pv = n \frac{N}{R} T = nkT$, the final expression for the entropy S is obtained as follows :

$$S = kn \left[\frac{5}{2} \log T - \log p + \log \frac{(2\pi m)^{\frac{3}{2}} e^{\frac{5}{2}} k^{\frac{3}{2}}}{h^3} \right].\dagger$$

This result should be compared with that obtained by classical methods, namely :

$$\text{entropy per molecule} = k \left[\frac{5}{2} \log T - \log p \right].$$

Thus, in this way Fermi and other workers (Tetrode and Stern) have succeeded in arriving at an absolute expression for the entropy, and have determined the value of the additive constant required by quantum theory.

One further observation is desirable. If, in quantising the

* By Stirling's formula,

$$n! = (2\pi n)^{\frac{1}{2}} \left(\frac{n}{e} \right)^n,$$

and hence

$$\log n! = n \log n - n + \frac{1}{2} \log (2\pi n),$$

or, to a high degree of accuracy, for large n ,

$$\log n! = n \log n - n$$

which implies

$$n! = \left(\frac{n}{e} \right)^n \text{ or } \frac{n!}{n^n} = e^{-n}.$$

† A slight modification of this formula is necessary to take account of the so-called *statistical weight* P of the atom in its fundamental state. Each energy level is in reality the superposition of $2j + 1$ levels which split up when the atom is in a magnetic field. An amount $kn \log P$ must therefore be added to the entropy. For the alkali metals $P = 2$ since $j = \frac{1}{2}$. For the electron, the statistical weight is 2, the electron being able to assume two orientations.

system, the gaseous mass had been divided into cells containing two or more molecules, a different result would have been obtained because the probability P would be different. This suggested to Fermi the idea that Sommerfeld's simple law for quantising a system by equating the integrals $\int p dq$ to whole number multiples of h , might not be valid for systems containing several identical particles, as, for example, the helium atom with its two indistinguishable electrons.

This idea also suggests itself from the simple consideration of a rotating ring composed of three equally-spaced electrons. If p is the momentum of the rotating system, to quantise by Sommerfeld's rule, we put $2\pi p = nh$. In reality, however, the system recurs, *i.e.*, becomes completely identical with its initial state, after a rotation of only $\frac{2\pi}{3}$, and it may be urged that the quantisation

rule $\int p dq = nh$ should be applied to give $\frac{2\pi}{3} p = nh$. Thus, two divergent results are obtained. Arguments of this kind, together with the calculation of the entropy, were given by Fermi in 1924, and represented the first steps towards Pauli's *exclusion principle*.

The New Statistical Mechanics for Material Particles (Fermi-Dirac)

It is clear from what has been said in the previous section, that, in calculating the energy and entropy of a gas, it is the quantum theory which dominates the argument, and not classical mechanics. Maxwell's law, Boltzmann's statistics, the theory of the specific heats of gases, in fact, the whole edifice erected before the introduction of Planck's discontinuity concept, are subject to a correction. The energy distribution in the black body spectrum was obtained by *quantising* the motion of oscillators capable of emitting and absorbing energy in finite steps, and in this way the experimental facts were faithfully reproduced. This distribution departs sensibly from that deduced from the classical theory only at low temperatures. In the same way, in quantising the perfect gas, we shall arrive at a result which differs from the classical form,

only as we approach low temperatures, high pressures or, in other words, highly condensed states, for which, as we say, there is *degeneracy of the perfect gas*. That this is as it should be is shown by the fact that it is only at low temperatures that the specific heats of monatomic gases at constant volume tend to decrease, classical thermodynamics predicting for the perfect monatomic gas, the result $C_v = 3R$, that is to say, a molecular specific heat independent of temperature.

Thus the behaviour of a perfect gas at temperatures near the absolute zero and at high pressures represents a case of degeneracy. It is important to discover the equation of state appropriate to degeneracy, the statistics which replace those of Maxwell, and the values of the energy and the entropy, all of which are of course closely interrelated concepts.

Unfortunately, however, as in practice, the deviations due to the degeneracy of the gas, although not actually negligible, are always smaller than those due to the actual gas not being perfect, the *deviations of the former kind are masked by the effect of the latter*.

* We pass on to Fermi's calculations leading to relations which take the place of those appropriate to the perfect gas of classical mechanics.

The equation of state of the perfect gas can be written $p = n \frac{R}{N} T$, expressing the fact that the pressure is proportional to the temperature, and to the number of molecules present per cm^3 (more briefly $p = nkT$).

To find the total energy of the gaseous mass, the motion of the molecules must be quantised. How this can be done has already been seen in the preceding section where the determination of the absolute entropy was outlined.

We imagine the molecules constrained by a suitable dynamical field, as so many spatial oscillators, in other words, mass points which oscillate about a fixed centre which attracts them with a force proportional to the displacement. A space oscillator of this kind of frequency ν is defined by three quantum numbers s_1, s_2, s_3 , and the energy of the molecule is expressed by :

$$W = h\nu(s_1 + s_2 + s_3) = h\nu s.$$

The force acting, when the molecule is at the distance r from the centre of attraction, is $4\pi^2\nu^2mr$ and the potential energy of this force of attraction is the integral of the force, $2\pi^2\nu^2mr^2$.

Putting $s = s_1 + s_2 + s_3$ there are $Q = \frac{(s+1)(s+2)}{2}$ sets of values of s_1, s_2, s_3 for a given value of s . For example, if $s = 2$ there are possible the combinations 200, 020, 002, 110, 101, 011, for s_1, s_2, s_3 . Thus the greater the sum s , the more numerous the ways of assigning the three quantum numbers s_1, s_2, s_3 to give this sum.

An important rule due to the physicist Pauli of Hamburg was established

in 1925, as an addition to Sommerfeld's rules. The rule states that in an atom containing an electron whose motion is defined by four quantum numbers, there cannot exist another electron to which these same quantum numbers apply. This is the same as saying that in a given orbit there can be one electron and one electron only (see p. 139).

Thus Pauli's principle asserts that in an atom there exists in each completely defined quantum condition at most one electron. Pauli was able to show that the structure of complex spectra is dominated by this principle.

Fermi took the bold course of transferring the rule to the collection of molecules forming a gaseous mass, before the principle itself had been extended to the electrons contained within a *molecule* (Heitler and London, 1927). This implies nothing less than the assumption that the molecules are associated in such a way that a given quantum state is occupied by at most one molecule.

We may point out, to help make the matter clear, that the Pauli-Fermi idea corresponds to a philosophical principle of nature, namely the principle of variety. However many objects of the "same type" which can be grouped together as one unity, there will in reality be no two objects the same in all respects, and this is true without limit. All the grains of rice produced in a rice field are different, in volume, weight, etc. The innumerable totality of the products of all rice fields contains no two grains which do not differ one from the other in some particular. In a whole nation there are no two equal individuals. In the present case, on account of the quantum theory the difference in question is an abrupt change.

Applying Pauli's principle to the problem under consideration, we must assume that in the gaseous mass there are no two molecules with the same quantum numbers, so that there will be at most $Q_s = \frac{(s+1)(s+2)}{2}$

molecules in the state s . Hence there will be at most one molecule of zero energy, three with energy $h\nu$, seven with energy $2h\nu$, and so on. The main problem is now to find how the total energy of the gas, W , starting from the absolute zero, is distributed among the N molecules. Let there be N_s molecules of energy $sh\nu$. We can write down at once that the sum of all the groups N_s will equal the total number of molecules N , and that the sum of their energies $sh\nu N_s$ will equal the total energy $Eh\nu$. These conditions are :

$$\Sigma N_g = N \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\Sigma s N_s = E \quad (2)$$

The number of molecules N_s which have energy $sh\nu$ will be equal or less than Q_s , the *maximum* number of sets of values s_1, s_2, s_3 such that $s_1 + s_2 + s_3 = s$. If, for example, $N_s = 15$ and $Q_s = 21$, there will be many possible modes of existence of the gas without its state being altered. The number of such complexions will equal the number of ways of arranging 15 objects among 21 positions. This number will measure the probability of the state, only in respect of molecules of the species s . What matters, however, is the combined or *simultaneous* probability of all the groups, and this is given by the product of the individual probabilities. The determination of the actual state of the gas means the determination of the most probable state, for Nature is such that any system tends to "evolve" towards the most probable states, which are the most frequently occurring.

Expressing mathematically the fact that all values of N_s must be such that their simultaneous existence determines a state of maximum probability we find that the most probable values of the N_s 's are related to the respective Q_s 's by the equation :

$$N_s = Q_s \frac{\alpha e^{-\beta s}}{1 + \alpha e^{-\beta s}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

in which α and β are constants. There must be two constants because the problem is defined by specifying the total number of molecules and the total energy they possess. It is from these two data that the most probable distribution is derived. Using (1), (2), and (3) we obtain :

$$N = \sum_{s=0}^{\infty} Q_s \frac{\alpha e^{-\beta s}}{1 + \alpha e^{-\beta s}}$$

$$E = \sum_{s=0}^{\infty} s Q_s \frac{\alpha e^{-\beta s}}{1 + \alpha e^{-\beta s}}.$$

Returning to the consideration of the molecules regarded as oscillators, we calculate the number s of molecules which possess *kinetic energy* between ϵ and $\epsilon + d\epsilon$, and which are situated at a distance r from the attracting centre. The total energy of one such molecule is the sum of the potential energy $2\pi^2\nu^2mr^2$ and of ϵ . Clearly, $ds = \frac{d\epsilon}{h\nu}$.

The motion of a molecule is completely defined by its three quantum numbers, and its co-ordinates at a given instant are functions of the latter :

$$x = \sqrt{Hs_1} \cos(2\pi\nu t - \alpha_1)$$

$$y = \sqrt{Hs_2} \cos(2\pi\nu t - \alpha_2)$$

where

$$H = \frac{h}{2\pi^2\nu m}$$

and an analogous expression for z . $\alpha_1, \alpha_2, \alpha_3$ represent three phase constants.

It is now easy to calculate the probability that a molecule of quantum numbers s_1, s_2, s_3 will be situated inside an elementary parallel-sided cell $dx dy dz$ at the point $x y z$, and then to pass to the probability—a much greater one—which applies for all molecules in this elementary volume having the quantum number sum s .

Multiplying this result by N_s we obtain the total number of molecules of the type s contained in the given volume element, and hence the density, that is, the number of molecules per unit volume at the point $x y z$. We, however, are interested in the density n_s appropriate to the point distant r from the attracting centre, and this follows easily from the preceding result, by a double integration in which account is taken of the relation $x^2 + y^2 + z^2 = r^2$.

The final result is as follows :

$$\text{density } n_s = \frac{2}{\pi^2 H^2} \frac{\alpha e^{-\beta s}}{1 + \alpha e^{-\beta s}} \sqrt{Hs - r^2}.$$

We form the product $n_s ds$, i.e., the product of the interval ds , and the number of molecules in unit volume which have quantum sums comprised between s and $(s + ds)$. As the quantum sum is proportional to the energy, it is clear that $n_s ds$ is the differential of the numerical distribution of the molecules with respect to their kinetic energy.

Now, as we know, Maxwell's law determines the statistical distribution in terms of the kinetic energy, and gives the number of molecules with velocities lying between c and $c + dc$ in accordance with the formula :

$$n_1 = 4n \sqrt{\frac{h^3 m^3}{\pi}} e^{-hmc^2} c^2 dc.$$

As $\frac{mc^2}{2} = \epsilon$ and therefore $mc dc = d\epsilon$, this may be written :

$$\text{Maxwellian Statistics : } n^*(\epsilon) d\epsilon = b \sqrt{\epsilon} e^{-\epsilon/k'T} d\epsilon. \quad . \quad . \quad . \quad (4)$$

where b is a constant.

This, then, is the statistical distribution of Maxwell. Fermi's statistics, which takes account of the *quantisation* of the energy, leads to a different result which is obtained from the calculation outlined above, and takes the form :

$$n(L)dL = n_s ds = n_s \frac{d\epsilon}{d\nu} = \frac{2}{\pi^2 H^2} \frac{\alpha e^{-\beta s}}{1 + \alpha e^{-\beta s}} \sqrt{Hs - r} \frac{d\epsilon}{d\nu} \quad . \quad . \quad (5)$$

where for s its value $\frac{\epsilon}{h\nu} + \frac{2\pi^2 \nu m}{h} r^2$ is to be substituted.

It should be noted at this point that Fermi's distribution reduces to the Maxwellian form when r tends to infinity, and, by comparing (4) and (5) it is clear that β must equal $h\nu/kT$. This relation serves to eliminate ν , which was merely an auxiliary quantity and ought not to appear in the final result.

To obtain the general relation between p , n , T , we must eliminate r from equation (5) and introduce n . This is accomplished using :

$$n = \int_0^\infty n(\epsilon) d\epsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and remembering that the pressure p is related to the mean kinetic energy ϵ_m of the molecules, by the formula :

$$p = \frac{2}{3} n \cdot \epsilon_m = \frac{2}{3} n \cdot \frac{1}{n} \int_0^\infty \epsilon n(\epsilon) d\epsilon \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

It is obvious that when the integrations have been performed in (6) and (7), r can be eliminated from these equations and the final result so obtained will be the desired relation between the pressure p , the temperature T and the density n . The calculations are somewhat laborious and involve development in series, and for further details the reader should consult Fermi's paper in the *Zeitschrift für Physik*, 11-12 (1926).

In the region of weak degeneracy, that is, when T is rather high and n is small, it is found that :

$$\text{pressure} \quad p = nkT \left\{ 1 + \frac{1}{16} \frac{h^3 n}{(\pi m k T)^{3/2}} + \dots \right\} \quad . \quad . \quad (8)$$

where $k = \frac{R}{N}$. It is apparent that the pressure exceeds the value given by the classical equation of state, $p = nkT$.

The second term in the brackets is ordinarily small, but if the density is very high and, at the same time, the temperature is reduced to a very low value, this term may become appreciable. For example, with helium at 5° absolute and at a pressure of 7 atmospheres, the deviation from the classical result ($p = nkT$) amounts to about 10%.

In the region of marked degeneracy the determination of the kinetic energy, the specific heat and the entropy, is of special

interest. All the necessary data are available and the calculations can easily be made. We obtain :

$$\text{pressure } p = \frac{1}{20} \sqrt[3]{\left(\frac{6}{\pi}\right)^2 \frac{h^2 n^{5/3}}{m}} + \sqrt[3]{\frac{16\pi^8}{3^5} \frac{mn^{\frac{1}{3}} k^2 T^2}{h^2}} + \dots \quad (9)$$

mean kinetic energy of the molecule

$$\bar{\epsilon} = \frac{3}{40} \sqrt[3]{\frac{36}{\pi^2} \frac{h^2 n^{\frac{2}{3}}}{m}} + \sqrt[3]{\frac{2\pi^8}{9} \frac{mk^2 T^2}{h^2 n^{\frac{2}{3}}}} + \dots \quad (10)$$

The remarkable result which emerges from these formulæ is that at the lowest temperatures ($T = 0$), both the pressure and the kinetic energy approach limiting values.

The specific heat at constant volume $C_v = \frac{d\bar{\epsilon}}{dT}$ is obtained at once by differentiating (10).

We have :

$$C_v = \frac{d\bar{\epsilon}}{dT} = \sqrt[3]{\frac{16\pi^8}{9} \frac{mk^2 T}{h^2 n^{\frac{2}{3}}}} \dots \quad (11)$$

The specific heat vanishes at the absolute zero.

Finally the entropy S is obtained directly from its definition,

$$S = n \int_0^T \frac{d\bar{\epsilon}}{T}.$$

Entropy of n molecules :

$$S = nk \left[\frac{3}{2} \log T - \log n + \log \frac{(2\pi mk)^{\frac{3}{2}} e^{\frac{5}{2}}}{h^3} \right] \dots \quad (12)$$

which agrees exactly with the result of Tetrode, Stern and Sackur.

Thus quantum mechanics leads to an important result for the entropy. Whereas classical thermodynamics does not yield a value for the so-called entropy constant,* that is to say, it is able to deal with differences of entropy only, quantum mechanics

* We recall that in classical thermodynamics we use for the definition of entropy, the relation

$$dS = \frac{dQ}{T},$$

which is valid for reversible transformations. This determines S save for an additive constant which is termed the entropy constant.

asserts that the entropy is zero at $T = 0$ and maintains this to be true, whatever the state of aggregation of the substance. This result is an extension of the so-called Nernst principle (Third Law of Thermodynamics) which affirms that the *variation* of entropy in a transformation involving solid or liquid substances (the so-called condensed phases), is *nil* at the absolute zero. We now see that this principle deduced by Nernst on an experimental basis is extended and completed in the sense* that not only is the *variation* of the entropy *nil* at the absolute zero, but also the entropy itself vanishes.

$$\left(S = 0 \text{ for } T = 0 \text{ and not merely } \frac{\partial S}{\partial T} = 0 \text{ for } T = 0 \right).$$

These ideas of Fermi have had repercussions of the greatest importance, and mark the first step towards a new horizon in physical research. Numerous applications are to be found in the papers of Fermi and other workers.

The Statistics of Boltzmann and Fermi Compared

We have examined the two statistical distribution laws, namely, Maxwell's law valid for a perfect gas :

$$n^*(\epsilon)d\epsilon = b\sqrt{\epsilon} d\epsilon e^{-\epsilon/kT} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

(ϵ is the kinetic energy)

and Fermi's more general result, which is valid also for a gas in the degenerate state :

$$n(\epsilon)d\epsilon = 2\pi \frac{(2m)^{\frac{3}{2}}}{h^3} \sqrt{\epsilon} d\epsilon \frac{1}{\frac{1}{A} e^{\epsilon/kT} + 1} \quad . \quad . \quad . \quad (2)$$

The salient difference between the two statistics is that, whilst for the Maxwellian law the molecular energy is proportional to the temperature of the gas, according to Fermi's statistics, in the state of complete degeneracy, the energy (and also the pressure) is approximately independent of temperature. In short, at the absolute zero, thanks to the *exclusion* principle according to which not more than one atom can have zero energy, the great majority

* Planck's interpretation.

of the atoms are constrained to occupy states of higher energy. The gas must therefore possess non-zero energy E_0 and a non-zero pressure p_0 , even at the absolute zero. Fig. 77 shows the energy of the gas as a function of temperature.

We observe that A has the dimensions of a pure number. It is upon the magnitude of A that the degree of degeneracy depends.

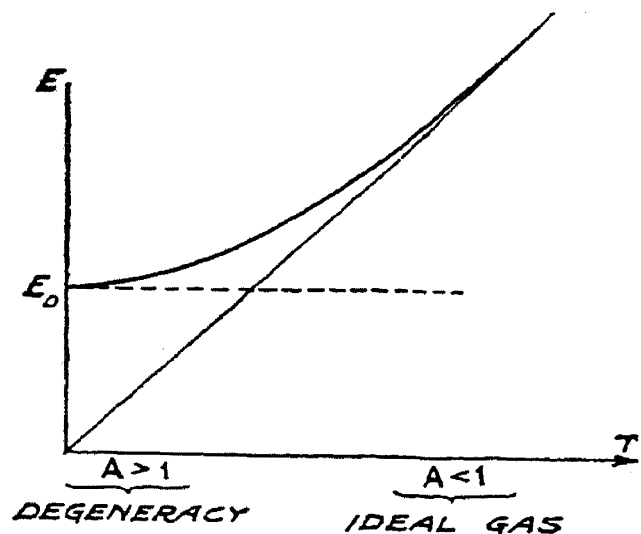


FIG. 77.

As Fermi's calculations involve developments in series which are only valid in restricted domains of the variable parameters, Fermi gives results for the two cases corresponding respectively to weak and pronounced degeneracy. It should be remembered, of course, that both sets of results apply to the same problem although each is limited to a restricted range.

When A has a value small compared with unity, (2) reduces to the Maxwellian law so that for $A \ll 1$ we have the ideal gas.

Stripped of unessentials, the Maxwellian function for the statistical distribution is characterised by the presence of the factor $e^{-\epsilon/kT}$, which gives the probability of a state, whereas the more general function of Fermi takes the form :

$$f = \frac{1}{\frac{1}{A} e^{\epsilon/kT} + 1}.$$

The *criterion of degeneracy* depends on the value of A . Small values of A imply classical conditions, large values correspond to complete degeneracy. The value of A is fixed by the atomic mass of the gas, the temperature and the density, and these three quantities therefore will determine the criterion of degeneracy. An inspection of Fermi's formula,

$$p = nkT \left[1 + \frac{1}{16} \frac{h^3 n}{(\pi m k T)^{3/2}} + \dots \right]$$

shows immediately that the criterion in question will be based on the magnitude of $\frac{n}{(mT)^{\frac{3}{2}}}$. The detailed calculation establishes that the *absolute criterion of degeneracy* is the excess or defect of the quantity $A = \frac{nh^3}{2(2\pi mkT)^{\frac{3}{2}}}$ with respect to unity.

When $\frac{nh^3}{2(2\pi mkT)^{\frac{3}{2}}} > 1$ there is degeneracy

and when $\frac{nh^3}{2(2\pi mkT)^{\frac{3}{2}}} < 1$ there is no degeneracy.

Thus, if $A = \frac{nh^3}{2(2\pi mkT)^{\frac{3}{2}}}$ * is not very small compared with unity, then even if the gas is still considered to be perfect, that is to say, if the volumes of the molecules and the inter-molecular forces are neglected, we must regard the motion of the molecules as subject to quantum laws. The gas in this condition is *degenerate*.

For hydrogen at normal temperature and pressure, A is of the order of *one thousandth*, and there is therefore no question of degeneracy.

It is clear that as three variables determine A , the gas can become degenerate in three different ways :

(a) When the temperature T is very low, for example, 3° — 4° abs., and the pressure equals several atmospheres. With the technical difficulties of experiments to test the theory must be coupled the fact that under these conditions the gas can no longer be considered perfect because mutual forces between the molecules come into play.

(b) When the number of molecules per cm^3 is very large. This condition is realised in certain stars, where the density attains a value of 10^5 , so that the gas is degenerate despite the very high temperature.

(c) When the mass m is small. This is the case for the electron gas in metals, which we shall shortly discuss.

It is at once clear that on account of the small value of

* These values of A are for electron gas. With an ordinary gas the factor 2 in the denominator is absent.

m (9×10^{-28} gm.) electron gas is in a condition of degeneracy even at ordinary temperatures, provided we make the natural assumption that the number of conduction electrons equals the number of atoms.

Taking silver, for example, with atomic weight 107.9 and density 10.5, the number of atoms per unit volume is clearly,

$$\frac{10.5}{107.9} \times 60.6 \times 10^{22} = 5.9 \times 10^{22}.$$

Substituting in the expression for A this value of n and the known values of m , k , and h ,

$$m = 9 \times 10^{-28}$$

$$k = 13.7 \times 10^{-17}$$

$$h = 6.55 \times 10^{-27},$$

and considering ordinary temperatures ($T = 300^\circ$ abs.), we obtain $A = \frac{nh^3}{2(2\pi mkT)^{\frac{3}{2}}} = 2,300$, *i.e.*, a very large number compared with unity. Thus in the assembly of conduction electrons in a metal we have to do with a definitely degenerate system.

We now turn to the consideration of the specific heat, which is given, *per electron*, by :

$$C_v = \pi^2 \frac{mk^2}{h^2} \left(\frac{8\pi}{3n} \right)^{\frac{2}{3}} T.$$

This tends to zero as T approaches the absolute zero of temperature (Nernst Law). We now calculate the specific heat appropriate to *unit volume* of the metal, assuming as before that the number of electrons equals the number of atoms (for silver, 5.9×10^{22} per cc.). We obtain, at the temperature $T = 300$ abs. :

$$C_v = \frac{\pi^2 mk}{h^2} \left(\frac{8\pi}{3n} \right)^{\frac{2}{3}} 300 R = 0.024 R.$$

This value for the specific heat is about 60 times smaller than that required by the classical theory which gives $C_v = \frac{2}{3} R$. Thus the difficulty referred to in Vol. I, p. 49, relating to the contribution which the electrons should make to the specific heat,

is removed because this contribution is now seen to be so small as to have no influence on the experimental values of C_v .

If we compare the curves representing the velocity distributions (f as function of v) of Fermi and Maxwell respectively, it is clear that the lower part of the Fermi curve resembles Maxwell's result. In other words, for the higher velocities there is no difference between the two statistics. Now the electrons corresponding to this part of the curve, being endowed with the highest velocities, are those which escape from the conductor, and, as a consequence, the escaping electrons will exhibit Maxwellian distribution outside the metal. Experiments by Richardson and others have, in fact,

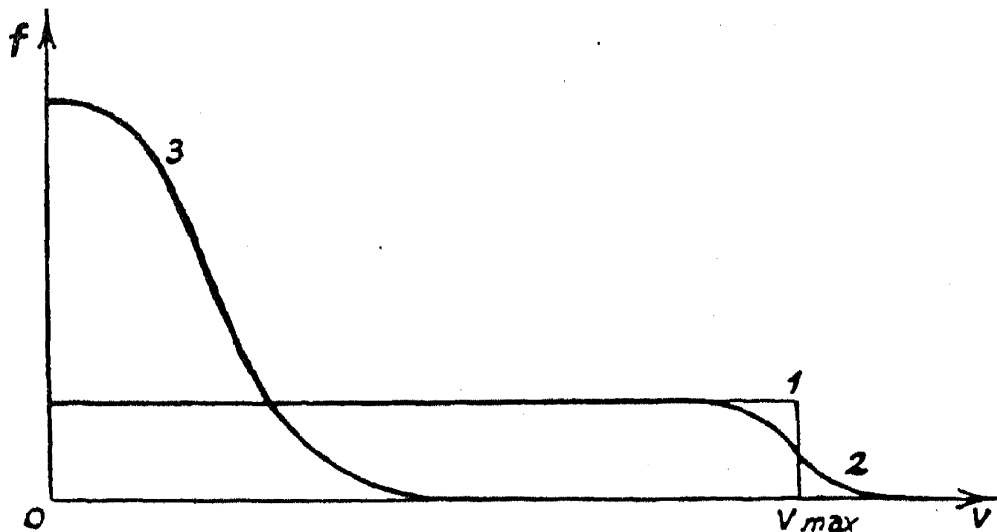


FIG. 78.

shown that the velocities of the electrons issuing from hot metals are distributed in accordance with classical statistics. In the interior, on the other hand, the velocity of the electrons remains independent of the temperature. The following further points are important :

(a) in Fermi's statistics at the absolute zero f is constant and the " curve " for f as a function of v reduces to a horizontal line which extends up to a value of the abscissa v equal to:

$$v_{\max} = \frac{h}{m} \sqrt[3]{\frac{3n}{4\pi}}.$$

(b) in Fermi's statistics, at temperatures a little higher than the absolute zero, f is given by a curve such as 2 (Fig. 78), and the

velocities in the extreme right-hand section of the curve represent a Maxwellian distribution.

(c) in Maxwell's statistics, represented in curve 3, the maximum *density* corresponds to the low velocities,

$$\left(\frac{nm^{\frac{3}{2}}}{(2\pi kT)^{\frac{3}{2}}} e^{-\frac{mv^2}{2kT}} \right).$$

It will be useful to summarise the formulæ representing Fermi's statistics.

$$f = \frac{G}{h^3} \frac{1}{A^{-1}e^{\epsilon/kT} + 1} \quad \dots \quad (\alpha)$$

ϵ = energy of the particle
 k = Boltzmann's constant
 $G = 2$ for electron gas

A is defined by the relation,

$$2mkT \cdot \log A = h^2 \left(\frac{3n}{4\pi G} \right)^{\frac{2}{3}} \text{ to a first approximation } \dots \quad (\beta)$$

Inserting this value of A into (α) we have :

$$f = \frac{G}{h^3} \frac{1}{e^{(\epsilon - W_i)/kT} + 1} \text{ where } W_i = \frac{h^2}{2m} \left(\frac{3n}{4\pi G} \right)^{\frac{2}{3}}.$$

To obtain the mean velocity \bar{v} and the mean square velocity \bar{v}^2 it is necessary to evaluate the integrals :

$$\frac{1}{n} \int v f(v) dv \text{ and } \frac{1}{n} \int v^2 f(v) dv$$

$$\text{which give } \dots \quad \bar{v} = \frac{3}{4} v_m \quad \bar{v}^2 = \frac{3}{5} v_m^2,$$

where $v_m = \frac{h}{m} \left(\frac{3n}{4\pi} \right)^{\frac{1}{3}}$ is the maximum velocity of the electrons at the absolute zero.

* The energy of the gas at the absolute zero can be easily calculated in the following manner. The energy of the system is, we know, a function of the quantum numbers and can therefore assume only discrete or *quantised* values. It has already been shown that a point molecule moving within a cube of side a and rebounding elastically from the walls, has for velocity components :

$$\xi = \pm \frac{n_1 h}{2ma} \quad \eta = \pm \frac{n_2 h}{2ma} \quad \zeta = \pm \frac{n_3 h}{2ma},$$

where n_1, n_2, n_3 are three whole numbers. The kinetic energy is given by

$$W = \frac{m}{2} (\xi^2 + \eta^2 + \zeta^2) = \frac{h^2}{8ma^2} (n_1^2 + n_2^2 + n_3^2).$$

The values which the energy can assume form a triply-infinite manifold. We now introduce Pauli's *exclusion principle*. Applied to the present problem, the principle affirms that there cannot be more than one molecule corresponding to a given set of values of n_1, n_2, n_3 . It follows at once that at the absolute zero the kinetic energy (and the pressure) of the gas must have a value different from zero. At the absolute zero the energy of the system is a minimum, and according to classical statistics all the molecules will be at rest. From the quantum standpoint and taking account of Pauli's

principle, for one molecule only will $n_1 = n_2 = n_3 = 0$, and hence $W = 0$. For one molecule $n_1 = n_2 = n_3 = 0$, but for three others,

$$\begin{array}{lll} n_1 = 1 & n_2 = 0 & n_3 = 0 \\ n_1 = 0 & n_2 = 1 & n_3 = 0 \\ n_1 = 0 & n_2 = 0 & n_3 = 1 \end{array}$$

and so on.

In velocity space we take as unit length $h/2ma$ so that the possible states of the molecules are represented by points having whole number co-ordinates. By Pauli's principle at each of these points will be found at most one molecule. At the absolute zero, that is, in the state of least energy, the representative points will occupy with uniform density, the positive octant of a sphere, outside which no representative points will be found. This is so because the quantum numbers of the molecules must have the lowest possible values and at the same time no two molecules can have the same set of quantum numbers. At temperatures above the absolute zero, the representative points of some molecules will lie outside the sphere, on account of the greater energy of these molecules. At high temperatures the representative points form a large and tenuous cloud, and a considerable number of the possible positions near the origin will be vacant.

In the region of not too low temperatures Pauli's principle produces no appreciable modification of the classical distribution, and it is clear that the Fermi statistics must at high temperatures give in the limit the same results as the classical laws—in other words, the *degeneracy of the gas* will disappear.

We will now calculate the maximum velocity v_{\max} at the absolute zero. The total number of possible positions in the octant is $\frac{1}{8} \cdot \frac{4}{3} \pi R^3$, and this also represents the total number of molecules. Hence,

$$\frac{1}{8} \cdot \frac{4}{3} \pi R^3 = n.$$

The radius of the sphere being measured in units $\frac{h}{2ma}$, the corresponding maximum velocity will be :

$$v_{\max} = R \cdot \frac{h}{2ma} = \frac{h}{m} \left(\frac{3n}{4\pi} \right)^{\frac{1}{3}}.$$

The corresponding kinetic energy has the value :

$$\frac{m}{2} v_{\max}^2 = \frac{h^2}{2m} \left(\frac{3n}{4\pi} \right)^{\frac{2}{3}}.$$

This is the quantity W_i met with above, the significance of which is now clear.

The Bose-Einstein Statistics and its Relation with those of Boltzmann and Fermi *

In this section we shall attempt to co-ordinate the new statistical conceptions. Up to this point, in discussing the work of Boltzmann and of Fermi, we have spoken only of matter, and no reference has been made to radiational energy. Actually, when in Chapter I it was explained how Planck arrived at his celebrated

* Bose, *Zeits f. Physik*, 26, p. 178, 1924, and 27, p. 38, 1925.

formula which has opened up a new era in physics, we were already introducing a *statistical* result. The aim of this branch of physics is, in fact, to give the law according to which the individuals forming an assembly are distributed among the possible values of their characteristic magnitude. The individuals in Planck's case were the "simple" radiations occupying the small frequency intervals ν to $(\nu + d\nu)$ and it was required to determine the intensity of each radiation as a function of its characteristic, *i.e.*, the frequency ν .

We shall now show how this result can be arrived at by a method precisely analogous to that which leads to the new statistics controlling the behaviour of gas molecules and electrons.

Bodies are made up of collections of "monads" (atoms or molecules), and radiation is also to be considered as composed of monads, known as light quants. When physicists found that it was necessary to ascribe *momentum* to light quants as well as to material particles, it occurred to them to apply to radiation the statistical methods which previously had been used only for gas problems. The fundamental problem to be solved was the following: how does the spectral distribution of the electromagnetic energy in the radiation emitted by an isothermal enclosure depend on the temperature?

It was proposed to regard the radiational energy of the enclosure as a *gas made up of light quants*, in which the possible values of the momentum $p = h\nu/c$ were distributed among the different individuals in accordance with a law similar to that obtaining for a material gas.

(I.) We begin with Boltzmann's statistics or, as it is also called, the *natural* statistics. To fix ideas, suppose the collection of monads to be equal material masses, subject to no forces, that is, we imagine an ideal gas, and enquire as to the numerical distributions of the monads according to their velocities.

To determine completely the state of the gas it is necessary to know not only the co-ordinates x, y, z of each molecule, but also the three conjugate momenta $p_1 = m\dot{x}, p_2 = m\dot{y}, p_3 = m\dot{z}$.

To obtain a single point representation of the state of a molecule, a hyper-space of 6 dimensions, one corresponding to each of the

6 elements indicated above, must be used. Imagine this "phase" space subdivided into a large number of very small cells similar in every respect. If the distribution of the molecules among these cells be known, then the state of the gaseous mass is completely determined.

Clearly from among all the conceivable distributions, the one which can be realised in the greatest possible number of ways will be the one which the gas will most probably assume. It is therefore necessary to know in how many ways a given distribution of the molecules can be realised. To this end it is sufficient merely to know the number of particles present in each cell, *without knowing which particular particles these may be*, supposing each particle to bear an identification mark.

We may adopt to begin with the obvious assumption that the particles are not related in any way one to another, so that the probability of a molecule being present in an elementary volume, is independent of the presence of another molecule in any other cell.

The number of complexions, or the thermodynamic probability, is then given by :

$$W = \frac{N!}{n_1! n_2! n_3! \dots},$$

as we have already seen. N is the total number of molecules, n_1, n_2, n_3, \dots are the numbers of molecules representing individual groups in which each molecule has energy given respectively by E_1, E_2, E_3, \dots

Thus $\Sigma n = N$ and $\Sigma n_i E_i = E_{\text{total}}$.

We observe that in Boltzmann's statistics there is one factor which remains undetermined—the volume of the elementary cell. The significance of this will be realised from what follows.

We return to the problem of the distribution of the gas molecules among the different cells for a given temperature of the gaseous mass. Remembering that at the given temperature a large number of complexions may be realised, and proceeding to the determination of the one which possesses the maximum probability, we shall, as the result of our calculations, be able to specify the

fraction of the N molecules present in a given cell of volume H . The procedure to be adopted is obvious. We are confronted in fact with a perfectly definite problem in the calculus of variations, the problem of stationary values. The distribution sought for must possess *maximum* probability, subject to the supplementary conditions that the total number of molecules and the total energy shall be those obtaining for the actual gas contained in volume V at temperature T . The character of the gas is also fixed by the value assigned to the particle mass m .

The solution of the problem presents no particular difficulty, and we give the result :

elementary probability for a molecule to have velocity components $\dot{x}_i, \dot{y}_i, \dot{z}_i$:

$$w_i = \frac{n_i}{N} = \frac{H}{V} (2\pi m k T)^{\frac{3}{2}} e^{-\frac{m}{2kT}(\dot{x}_i^2 + \dot{y}_i^2 + \dot{z}_i^2)}$$

or, more simply,

$$w_i = b e^{-\frac{mv^2}{2kT}} = b e^{-\epsilon_i/kT}.$$

This is the Maxwellian distribution.

The method of carrying out calculations of this kind has already been briefly indicated in discussing Fermi's statistics. It should be noted that the probability is not determined as regards absolute value, because it depends on the volume H of a cell.*

To conclude, Boltzmann obtained from his statistical investigation a definite physical interpretation of entropy, and a method for calculating its value. The entropy of any state is proportional—the constant of proportionality being $\frac{R}{N}$ —to the probability of realisation of the given state.

The reader's attention is here drawn to the following point. The properties of perfect gases are defined by the equation

* The elementary probability w_i is related, as already shown, to the total probability W by the equation $W = -\sum w_i \log w_i$, and the entropy S is $-kN \sum w_i \log w_i$. In the equilibrium state $dS = 0$. The latter equation expresses mathematically the *condition for an extreme value*, which is the essence of the problem.

Furthermore, the entropy is related to other thermodynamical functions (total energy, free energy, specific heat), and knowing the entropy the complete behaviour of the system is determined.

$pV = RT$, which follows from the laws of Boyle and Gay-Lussac. The total kinetic energy $\frac{Mc^2}{2}$ is then found to be $\frac{3}{2} RT$. We considered these results in Vol. I, Chap. III. Here, however, a second method of approach to the problem of the perfect gas has been obtained. The distribution law is determined which makes the probability of state of the gaseous mass a maximum. Then, from the equation connecting entropy and probability and using the thermodynamic definition of temperature $\left(\frac{3}{2} \frac{R}{N} T = \frac{1}{2} m C^2\right)$, the equation of the perfect gas $pV = RT$ is derived. This is the statistical method.

(II.) An outline of the Bose-Einstein statistics (1924) will now be given. Bose considers the radiation contained in an enclosure of volume V as made up of particles or light quanta of energy ϵ , for each of which Planck's celebrated relation $\epsilon = h\nu$ holds good where ν is the frequency. With each light quant of energy ϵ is associated the momentum $p = \frac{\epsilon}{c}$, and the components of this vector p satisfy the condition :

$$p_x^2 + p_y^2 + p_z^2 = \frac{\epsilon^2}{c^2}.$$

Thus a light quant will be completely determined when the three co-ordinates fixing its position in space and the three components of the momentum are known. It will be defined in fact by a point in the six-dimensional phase space, and the distribution in space of these points will give a complete representation of the composition of the radiational energy in the enclosure. We begin by determining the elementary volume in phase space, containing all points representing light quanta of energy between ϵ and $\epsilon + d\epsilon$. This volume (or rather hypervolume) is given by :

$$d \left(\frac{4}{3} \pi p^3 \right) \int_V dx \, dy \, dz = V \cdot 4\pi \frac{\epsilon^2}{c^3} d\epsilon,$$

since

$$\int dx \, dy \, dz = V \text{ and } dp^3 = d \left(\frac{\epsilon^3}{c^3} \right) = 3 \frac{\epsilon^2}{c^3} d\epsilon.$$

We observe now that the product $x \times m\dot{x}$ (length \times momentum) has the dimensions ML^2T^{-1} which are the dimensions of *action* (energy \times time). It follows that the dimensions of an elementary cell in phase space are those of action raised to the third power. As the volume of the cell has remained arbitrary up to now, we may put it equal to h^3 where h is Planck's constant which has the dimensions of action. This step is closely connected with the fundamental notion of allowing the representative point to wander about in a restricted region of phase space, or expressed in another way, the assumption of indistinguishability of two points belonging to the same cell.

As has been seen, Heisenberg's principle indicates that the lowest possible value of the product of the errors associated with the simultaneous determination of two conjugate variables, is $h = 6.55 \times 10^{-27}$ erg sec.; $\Delta x \Delta p_x \geq h$. Recalling that a particle (light quant or electron) is defined by three pairs of conjugate co-ordinates, for each of which the above relation holds, it follows that :

$$\Delta p_x \Delta x \times \Delta p_y \Delta y \times \Delta p_z \Delta z = h^3.$$

In other words, in the phase space it is not possible to represent a particle as a point with exactly defined co-ordinates. Two states for which the representative points lie in the same cell are indistinguishable.

The number of cells containing quants of energy between ϵ and $(\epsilon + d\epsilon)$ is then

$$\Delta A = 4\pi V \frac{\epsilon^2 d\epsilon}{h^3 c^3}.$$

The fundamental concept in the Bose-Einstein statistics may now be stated in the following words. The definition of the probability of a distribution adopted in Boltzmann's statistics is not the only possible definition. The special properties of light quants lead to a *radical modification* in the computation of the *number of ways* of obtaining a given distribution, as well as in the actual concept of a "distribution." As a consequence the notion of entropy is also profoundly modified. Whereas in Boltzmann's statistics the *number of particles* n_i contained in a particular

cell, the i th, is computed, and the probability is defined by the formula of p. 371, in the Bose-Einstein statistics, we calculate the *number of cells* containing an assigned number K of particles.

Thus from among the total number of cells ΔA there will be $\Delta_0 A$ empty, $\Delta_1 A$ containing one "particle," $\Delta_2 A$ containing two, and so on. We shall speak of *any* assignment of values to, $\Delta_0 A, \Delta_1 A, \dots$ as a "distribution."

In how many ways then can it happen that there are $\Delta_0 A$ cells empty, $\Delta_1 A$ cells containing one particle, $\Delta_2 A$ cells containing two particles, etc. ?

This number of possibilities or number of distinct ways of realising a particular distribution is given by :

$$W = \frac{\Delta A!}{\Delta_0 A! \Delta_1 A! \Delta_2 A! \dots}$$

and among the various possible distributions the object is to find the one with maximum probability, which is the one which occurs in the greatest number of ways.

The association of an individuality with each particle is here given up. If the particles are distributed in groups contained in cells, each characterised by a particular energy value, then we shall consider two complexions as distinct if and only if the number of particles in one or more cells is not the same in the two cases.

Thus all the complexions which are derived from a given complexion by *permuting* the particles without changing the total number in each cell, form one case only.

As an example, suppose there are 4 cells and 5 particles to distribute among them. All the possible cases, 56 in number, are shown below :

Cell I.	.	.	5000	444	333	333	222	222	222
Cell II.	.	.	0500	100	200	110	300	221	001
Cell III.	.	.	0050	010	020	101	030	101	210
Cell IV.	.	.	0005	001	002	011	003	011	022

Cell I.	111	111	111	111	111	000	000	000000	0000	000
Cell II.	400	311	202	121	030	410	401	230032	1222	131
Cell III.	040	130	220	211	301	141	041	322300	2112	113
Cell IV.	004	003	022	112	113	004	114	003223	2121	311

Putting C for the number of cells, n for the number of objects to be distributed, then generally, according to the Bose-Einstein statistics, the total number of possible complexions is given by :

$$\frac{(n + C - 1)!}{n! (C - 1)!}$$

In our example :

$$\frac{(5 + 4 - 1)!}{5! 3!} = \frac{1, 2, 3, 4, 5, 6, 7, 8}{1, 2, 3, 4, 5, 6} = 56.$$

If the number of cells is sufficiently great the number of distinct complexions becomes :

$$\frac{(n + C)!}{n! C!}$$

Among all these cases we must determine those corresponding to a given "distribution" in the sense defined above. In the Bose-Einstein statistics, the *probability* W of a given distribution is defined as the number of different ways of obtaining it. This number is given by the formula reproduced on the preceding page.

Up to now the distribution of a single species of "particle" among the cells has been considered. The same reasoning can be repeated for light quants of other frequencies, and the total probability will be the product of the individual probabilities W . The most probable case is what we desire to know and to find it we make use of the *condition for a stationary value*, writing :

$$S (\text{entropy}) = k \log W,$$

condition of maximum probability,

$$d \log W = \text{zero}$$

subject to the conditions :

$$\begin{aligned} E_{\text{total}} &= \sum h\nu_i n_i \\ n &= \sum n_i. \end{aligned}$$

The solution of these equations yields a result which tells us the number of cells containing light quants of the type $h\nu$, the number containing light quants of the type $h\nu^1$, and so on. Expressed in another way, the results determine the distribution

of the total energy, as a function of the frequency ν . The energy ΔE contained in the volume V and belonging to light quanta of frequency between ν and $(\nu + d\nu)$ is shown to equal :

$$\Delta E = V 8\pi \frac{h\nu^3}{c^3} \frac{d\nu}{e^{\frac{h\nu}{kT}} - 1}.*$$

If Boltzmann's methods had been used instead, Rayleigh's formula † would have resulted.

(III.) Returning finally to Fermi's ideas, we are led to a third statistics. According to Bose, several light quanta may occupy the same cell in phase space. Fermi's postulate, on the other hand, is the following : *if a material particle* (the qualification "material" is introduced because Fermi's statistics is found to be applicable to matter whereas the Bose-Einstein result applies to radiational energy) *occupies a particular cell then no other particle can be present in the same cell. The cells are therefore empty or completely filled by one particle.* As pointed out earlier on, this notion is an extension of Pauli's exclusion principle which states that, if in an atom there is one electron characterised by the four quantum numbers n_1, n_2, n_3, n_4 , then there can be no other electron to which the same set of four values applies. Thus Fermi has extended the Pauli principle to matter.

Commencing with the calculation of the number of cells, it is

* For the detailed analysis see the original paper by Bose in the *Zeits. f. Physik*, 26, p. 178, 1924, or Bloch's book "L'ancienne et la nouvelle theorie des quanta," p. 392, 1930.

† The number of transverse vibrations which can be sustained in a volume V and of wave-length lying between λ and $\lambda + d\lambda$ we know to be (from Chapter IV.) $8\pi\lambda^{-4}d\lambda V$. Assuming equipartition of energy, to each vibration will correspond energy of total amount $\frac{R}{N} T$, appropriate to one degree of freedom. It follows that the energy ΔE is given by :

$$\Delta E = V 8\pi\lambda^{-4}d\lambda \frac{R}{N} T.$$

By definition,

$$\Delta E = \frac{8\pi}{c} E_\lambda d\lambda \cdot V$$

and hence

$$E_\lambda = c\lambda^{-4} \frac{R}{N} T,$$

which is Rayleigh's formula.

evident that the volume of phase space occupied by points for which the momentum lies between p and $(p + dp)$ is given by :

$$V \cdot d\left(\frac{4\pi}{3}p^3\right) = V4\pi p^2 dp.$$

The momentum is related to the energy E by the equation $E = \frac{p^2}{2m}$, and hence,

$$V \cdot 4\pi p^2 dp = 2\pi V(2m)^{\frac{3}{2}} E^{\frac{1}{2}} dE.$$

The number of cells, each of volume h^3 , is given by :

$$\Delta A = V \frac{2\pi}{h^3} (2m)^{\frac{3}{2}} E^{\frac{1}{2}} dE = \frac{4\pi}{h^3} m^3 v^2 dv.$$

The number of ways in which N molecules can be distributed among ΔA cells with not more than one molecule in one cell, is now evaluated. The number of different ways which may occur is :

$$W = \frac{\Delta A!}{N! (\Delta A - N)!}$$

and the distribution must be determined, which makes the total probability obtained by multiplying together the W 's a maximum. For example, suppose there are 5 cells, and 3 molecules : the number of possible complexions is $\frac{5!}{3! 2!} = 10$.

It is unnecessary to go into the purely mathematical details of the problem. The analysis leads to the determination of the entropy, and hence of the energy and specific heat. There are also obtained the new equation of state of the perfect gas and the theory of gas degeneracy. When the gas is far removed from the degenerate state, the results of the theory reduce to the familiar formulæ which are obtained by assuming classical properties and Maxwellian statistics. All this has been dealt with in an earlier section, but in the present discussion the matter is approached from a different standpoint.

At the present time we make use of two different statistics, one which allows the superposition of individuals in the same cell of phase space (Bose-Einstein) and which is valid for light quanta,

and another which forbids such superposition (Fermi-Dirac) and which is applicable to matter.

* The Thermal and Electrical Conductivities of Metals

In this and the two succeeding sections the application of Fermi's statistics to a number of important problems will be examined. We promised in Vol. I, Chap. VI, to return to the subject of the thermal and electrical conductivities of metals, to explain the important extension recently made by Sommerfeld (1927) at a time when Drude's thirty-year-old theory seemed to be in a state of collapse and appeared incapable of explaining experimental facts.

The principal successes of Riecke and Drude's theory, which regarded the transmission of heat and electricity as convection of electric particles, lay in the derivation of the Wiedemann-Franz law and in the general qualitative explanation of thermo-electric effects. The application by Lorentz, of Maxwellian statistics to the theory led, however, to a less good agreement with experimental data, in that the numerical coefficient in Drude's formula :

$$\frac{\text{thermal conductivity}}{\text{electrical conductivity}} = 3 \left(\frac{k}{e} \right)^2 T,$$

was computed to have the value 2 instead of 3. In addition, the theory was incapable of dealing with the questions of contact potential and the Volta series.

Finally, the serious difficulty was encountered that, according to the classical notion of equipartition of energy, the electrons should appropriate a considerable proportion of the thermal energy applied to the metal and should contribute materially to the specific heat, a conclusion in direct contradiction with experiment.

By an ingenious application of the Fermi-Dirac statistics to the old model of electrical and thermal conduction by electron convection, Sommerfeld has succeeded in removing these difficulties. We proceed to explain, although very briefly, the method by which Sommerfeld, basing his arguments on the new statistics, has reconstructed the old Drude theory of the electrons

which carry the electric current (pure electrical conductivity), and which pit themselves against the atom ions in the transfer of heat (pure thermal conductivity).

Sommerfeld's development of the theory depends on the assumption—which, moreover, can be shown to be true—that the electron gas responsible for the conduction properties, is already in a state of complete degeneracy at ordinary temperatures. As already explained, this comes about owing to the very small mass of the electron. Thus the statistical distribution law of the electrons which must be employed, is not the classical (Maxwellian) but the Fermi expression. The function $f(\xi, \eta, \zeta)$, giving the distribution in its dependence on the three velocity components, is symmetrical when there is no preferential flow of electrons in a particular direction. In that case f depends only on $v = \sqrt{\xi^2 + \eta^2 + \zeta^2}$, and not on the three velocity components taken separately.

If, however, there is an electric field in the direction of the x axis, along which the electric current flows (or if there is a temperature gradient in the x direction), then the distribution law of the electrons in unit volume is no longer symmetrical, and following Lorentz we can express the new distribution law in the form :

$$f = f_0 + \xi\theta,$$

where

$$\theta = -\frac{l}{v} \left(\frac{eF}{m} \frac{1}{v} \frac{\partial f_0}{\partial v} + \frac{\partial f_0}{\partial x} \right).$$

The function θ was arrived at by Lorentz * by an analysis of the paths traced out by electrons of velocity v and mean free path l , under the action of the electric force F and of collisions with atoms which were assumed to be stationary.

This, however, is not the fundamental point in the problem. The critical step is the assumption of the Fermi statistics in place of the Maxwellian law in determining f . Once this is done, the rest is merely mathematical development, in which we need only

* “Theory of Electrons,” (1909).

observe that in the case of pure electrical conduction, $\frac{\partial f_0}{\partial x} = 0$, and,

moreover, $\frac{\partial T}{\partial x} = 0$, since it is postulated that there is no temperature gradient along the conductor. In pure thermal conduction, the current I has the value zero.

For the practical resolution of the two problems we require the two fundamental magnitudes :

$$\text{Intensity of the electric current} \quad I = e \int \xi f d\omega$$

(per unit area and per second)

$$\text{Intensity of heat flow} \quad W = \frac{m}{2} \int \xi v^2 f d\omega.$$

Here $d\omega$ represents the volume element in the six-dimensional hyperspace of the representative points, thus :

$$d\omega = 4\pi \frac{m^3}{h^3} v^2 dv.*$$

$\xi f d\omega$ is therefore one of the elements which, when added together, give the total number of electrons passing. The reason for the integration is obvious. We shall not reproduce in detail Sommerfeld's very laborious calculations.

The electrical conductivity σ is, by definition; the ratio of the current I to the field F . Making the calculation Sommerfeld finds : †

<p><i>ideal gas</i></p> $\sigma = \frac{4}{3} \frac{e^2 l n}{\sqrt{2\pi m k T}}$	$ $	<p><i>completely degenerate gas</i></p> $\sigma = \frac{8\pi}{3} \frac{e^2 l}{h} \left(\frac{3n}{8\pi} \right)^{\frac{2}{3}}$
--	-----	--

The expression on the left obviously agrees, except for the numerical factor, with the classical result given by Drude. The other expression involves the quantum constant and is not explicitly a function of the temperature T .

The thermal conductivity C is also readily obtained. By

* See p. 378.

† *Zeits. f. Physik*, 1928,

definition, $W = -C \frac{\partial T}{\partial x}$, from which C can be derived. Sommerfeld finds, putting $F = 0$,

ideal gas $A \ll 1$

$$C = \frac{8}{3} \frac{\ln k \sqrt{kT}}{\sqrt{2\pi m}}$$

gas in state of degeneracy $A \gg 1$

$C = 0$ first order approximation,

$$C = \frac{8\pi^3}{9} \frac{lk^2T}{h} \left(\frac{3n}{8\pi}\right)^{3/2} \text{ second order approximation.}$$

The result $C = 0$ seems at first absurd, but its significance is clear when it is recalled that in the completely degenerate state the energy of the electrons is independent of temperature, and hence, in traversing a temperature gradient, there is no change in energy and no transmission of heat.

Forming the ratio of the two conductivities C/σ , the following values are obtained :

<i>ideal gas</i> $A \ll 1$ $\frac{C}{\sigma} = 2 \left(\frac{k}{e}\right)^2 T$	<i>gas in degenerate state</i> $A \gg 1$ $\frac{C}{\sigma} = \frac{\pi^2}{3} \left(\frac{k}{e}\right)^2 T.$
---	--

Drude's theory, on the other hand, gave the result $3 \left(\frac{k}{e}\right)^2 T$.

It is clear that we have again obtained the Wiedemann-Franz law, which affirms that the ratio of the conductivities is the same for all metals and is proportional to the absolute temperature. The sole difference between the present result and Drude's, lies in the value of the numerical coefficient, which now has the value $\frac{\pi^2}{3} = 3.3$ instead of 3.

Inserting the numerical values of the universal constant $k = 13.7 \times 10^{-17}$ and the electronic charge $e = 1.59 \times 10^{-20}$, we have for ordinary temperatures ($T = 300^\circ$):

$$\frac{\sigma}{C} = 7.1 \times 10^{-11},$$

and the average of the *experimental* values of the ratio (at 18° C.) for the twelve metals :

aluminium,	zinc,	nickel,
copper,	cadmium,	platinum,
silver,	lead,	palladium,
gold,	tin,	iron,

is equal to 7.11×10^{-11} .

Thus the new statistics provide a perfect explanation of the Wiedemann-Franz law, which has always been the corner-stone of speculations on the subject of the two conductivities.

Sommerfeld did not stop here but proceeded to an analysis of the Thomson effect, the Peltier effect, the Volta effect and the Richardson effect, as we shall show.

A further step forward in the theory of the conductivity of metals is contained in investigations by W. Houston. He regards the transportation of electric charge by electrons as the passage of the latter through the crystalline lattice and treats the problem mathematically with the aid of wave mechanics. We confine ourselves to giving a general idea of the theory and refer the reader to the original papers * for the details.

According to the fundamental principle of wave mechanics the motion of electrons can be followed only by interpreting in a certain way the propagation of waves associated symbolically with the electrons, the propagation of these waves being governed by a law similar to that which holds for light waves. The problem is now to investigate the reciprocal action of the waves associated with the moving electrons, and the ions of the crystalline lattice, which scatter the electron waves and cause them to interfere. The wave-length λ of the waves is several times larger than the lattice spacing.

No diffraction would occur if the ions of the metal were fixed, the electrons then having indefinitely large free path. The reason for this remarkable property lies in the regular periodic

* W. Houston, *Zeits. f. Physik*, 48, p. 449, 1928. *Phys. Rev.*, 15 July, 1929.

construction of the crystalline lattice constituting the metal (or its micro-crystals). The space lattice of the atoms gives rise to a periodic electric potential, which affects the electron waves in the same way as a dielectric medium of refractive index varying periodically from point to point affects waves of light. In optics it is shown that such a medium is transparent and does not scatter light. If, on the other hand, the ions are in a state of thermal agitation, the electron waves are scattered and become more attenuated with rise of temperature. From the corpuscular standpoint, this corresponds to a decrease in the mean free path of the electrons (diminished probability of unobstructed passage), and the electrical resistance increases as a consequence.†

Satisfactory quantitative results were obtained with this theory, and ultimately the phenomenon of superconductivity was also explained.

Another experimental fact, cleared up by the above considerations, is the lower conductivity of metallic alloys compared with that of the pure components. In alloys the atomic lattice is irregular, and this irregularity results in increased scattering of the electrons and, in consequence, the resistance is greater.

* The Thermionic Effect Treated by Quantum Statistics

In Vol. I, p. 185, we saw that Richardson, starting from the old notion of free electrons in a metal resembling the molecules of a gas and hence subject to Maxwellian statistics, had arrived at the following expression for the thermionic current :

$$I = aT^{\frac{1}{2}} e^{-b_0/kT}.$$

It will now be seen to what result the new statistics leads. We recall that the free electrons of the metal ("conduction electrons" for which the mean free path is several hundred times the inter-atomic distance) must be regarded as imprisoned in the

† To solve the problem it was necessary to elucidate two points : (a) the way in which the scattering depends on the amplitude of oscillation of the lattice particles ; (b) the law of variation with temperature of the amplitudes of vibration of these particles. Both these questions had previously been dealt with by Debye, and reference was made to (b) when we were discussing specific heats.

metal by a discontinuity in the electric potential at the surface. We know, in fact, that the electric potential undergoes an abrupt change when we pass from a point in the interior of the metal to a point just outside the surface. The inside potential is higher, so that electrons within the metal rebound from the surface and are unable to pass through unless their kinetic energy is sufficient to perform the work W_a required to carry a charge e to the exterior through a potential difference $V_a = \frac{1}{e} W_a$. This difference of

potential V_a is termed the *intrinsic potential* of the metal, and the corresponding work W_a is known as the *exit work* or *work function*.

The calculation of the *saturation current density* emitted by a metal at temperature T , is obtained in Sommerfeld's theory in precisely the same way as in the classical theory of Richardson. All that needs to be done is to substitute the Fermi distribution law (for degenerate electron gas) in the calculation, in place of the Boltzmann result.

The thermionic saturation current density is given by the number of electrons emitted per second from unit area of the surface of the metal, multiplied by the electron charge e . As in the classical theory, this current is equal to,

$$I = e \int_{\xi_0}^{\infty} d\xi \int_{-\infty}^{+\infty} d\eta \int_{-\infty}^{+\infty} \xi f d\zeta \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where $f = 2 \left(\frac{m}{h} \right)^3 \frac{1}{A^{-1} e^{\epsilon/kT} + 1} = 2 \left(\frac{m}{h} \right)^3 \frac{1}{e^{\frac{\epsilon - W_i}{kT}} + 1}$

and $W_i = \frac{h^2}{2m} \left(\frac{3n}{8\pi} \right)^{\frac{2}{3}}$

The lower limit for the velocity normal to the emitting surface (perpendicular to the x axis) is ξ_0 defined by the equation :

exit work $W_a = \frac{m \xi_0^2}{2}$

Performing the integration it is found that,

$$I = en \sqrt{\frac{kT}{2\pi m}} e^{-W_a/kT} = a T^{\frac{1}{2}} e^{-b_0/kT} \quad . \quad . \quad . \quad . \quad (2)$$

if there is no degeneracy, and

$$I = \frac{4\pi em}{h^3} (kT)^2 e^{-\frac{W_a - W_i}{kT}} \dots \dots \dots (3)$$

when there is complete degeneracy.

The latter result may be written more simply

$$I = AT^2 e^{-b/kT},$$

where $b = W_a - W_i$ and A is a constant independent of the particular emitting metal. b varies from element to element.

What is the physical significance of the quantity W_i which is subtracted from the total work W_a in the exponential term of (3)? W_i is the maximum kinetic energy and equals $5/3$ times the average kinetic energy of an electron at the absolute zero, a result which follows from the discussion on p. 368.

In the final result neither W_i nor the total work W_a appears but only their difference. As this same difference is met with in the photoelectric and Volta effects, it is clear that the three phenomena are very closely related.

From the formula :

$$W_i = \frac{m}{2} v_{\max}^2 = eV_i,$$

which expresses the equality at the absolute zero, of the energy corresponding to maximum velocity, and the energy *charge \times volts*, we can derive the potential V_i , which differs from that observed experimentally. The work function given by experiment is $W_a - W_i$.

From $\frac{m}{2} v_{\max}^2 = eV_i$ we have for silver,

$$v_{\max} = \frac{h}{m} \sqrt[3]{\frac{3n}{4\pi}} \qquad n = 5.9 \times 10^{22}$$

$$\therefore V_i = 5.6 \text{ volts for silver.}$$

For potassium and sodium the potential V_i has the values 2.1 and 3.2 volts respectively.

Thus in the case of silver the potential discontinuity at the surface exceeds by 5.6 volts the value which would be deduced by applying Maxwellian statistics to the electron gas.

Thermionic phenomena alone however do not allow us to decide between the old and the new theory, *i.e.*, whether the law

$$i = AT^{\frac{1}{2}} e^{-W_a/kT}$$

is valid, or the other law,

$$i = BT^2 e^{-\frac{W_a - W_i}{kT}}.$$

To reach a decision it is necessary to determine W_i by another method. Now, decisive proof of the validity of Fermi's statistics is forthcoming from experiments on electron diffraction. These have in fact enabled the intrinsic potential W_a to be measured directly for different metals. Thus for nickel it is found that $W_a = 16$ volts. W_i can be calculated and the constant b is measured in the thermionic effect. The relation $W_a - W_i = b$ is found to be approximately correct.

*The Volta Effect and the New Statistics

Turning now to the Volta effect, consider a condenser consisting of two parallel plates (Fig. 79) of different metals (copper and zinc, for example) and let the plates be connected together in vacuo by a wire of the same material as one of them. In the figure (Fig. 79) the plates are shown in contact at CC. Suppose an electron at an internal point A moved through the contact to the point B of the other plate, and then transferred across the evacuated space between the two plates and restored to its original position. The total work done is *nil*, and hence the algebraic sum of the potential discontinuities at the metal-vacuum contacts and at the contact CC between the two metals, will be zero. The Volta effect is the name given to the phenomenon which consists in the appearance of an electric field in the dielectric surrounding the two metals in contact. The measure of the effect is, by definition, the potential difference $V_1 - V_2$ between the points 1 and 2 situated just

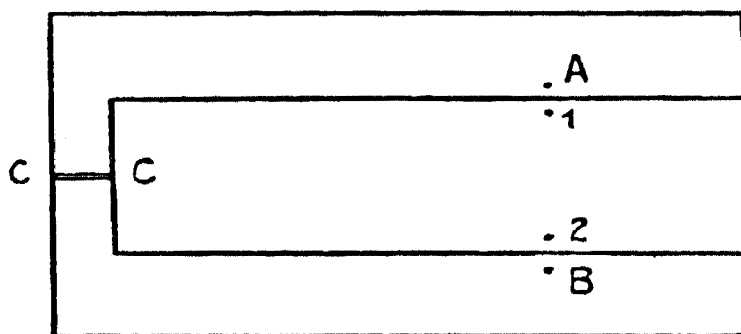


FIG. 79.

outside the surfaces of the respective metals. Denoting the potential difference at the contact CC by V it is clear that the following equation will hold good :

$$V_1 - V_2 = \frac{1}{e} W_{aB} + V - \frac{1}{e} W_{aA},$$

where $\frac{1}{e} W_{aA}$ and $\frac{1}{e} W_{aB}$ are the intrinsic potentials of the metals A and B respectively.

Sommerfeld's theory leads to the conclusion that the difference of potential at the bimetallic contact satisfies the relation :

$$eV = W_{iA} - W_{iB}.$$

This difference is of the order of several volts. Combining the two relations which have been obtained, the following equation for the Volta effect is arrived at :

$$e(V_1 - V_2) = (W_{aB} - W_{iB}) - (W_{aA} - W_{iA}) = b_B - b_A.$$

The difference of potential $V_1 - V_2$ (Volta effect) is equal (except for the factor e) to the difference in the values of the constant b corresponding to the two metals in Richardson's equation.

The direct connection between the photo-electric and the thermionic effects, which theoretically involve the same effective exit work, is difficult to establish experimentally because the substances from which photo-electric currents are easily obtained, are the alkali metals which melt and volatilise readily with rise of temperature, making it very difficult to investigate their thermionic properties. Conversely, those metals (tungsten, platinum) whose thermionic emission has been studied are insensitive to ordinary light and only begin to emit electrons in the ultra-violet where the experiments are difficult to carry out. There is, furthermore, the fundamental difficulty that photo-electric measurements must be confined to temperatures at which the thermionic emission current is imperceptible.

Paramagnetism of the Alkali Metals (Sodium, Potassium, Cæsium, Rubidium)

Many metals are paramagnetic, and among these are the alkali metals. It is known from spectroscopic evidence that for the

alkali metals the ions forming the crystalline lattice are devoid of magnetic moment, that is to say, they are diamagnetic. Thus the whole of the paramagnetism of the alkali metals must be due to the free electrons.

We recall that in Langevin's original theory (p. 236) it was assumed that, owing to thermal motion, the particles tend to orientate themselves either parallel or antiparallel to the field direction. The effect of the field was to produce an excess of particles with their magnetic moments parallel to the field direction, but with rise of temperature, the numbers of parallel and antiparallel particles tended to equality. Applying *classical statistics* it was found that the magnetic susceptibility varied inversely as the absolute temperature, a result which is confirmed by experiment in the case of ordinary gases. For the alkali metals, however, Pauli * found it necessary to consider the electron gas, for which the elementary magnetic moment is,

$$\frac{eh}{4\pi mc} = 0.91 \times 10^{-20} \frac{\text{erg}}{\text{gauss}},$$

as subject to the Fermi distribution law. He deduced an expression for the susceptibility which, to a first approximation, is a constant independent of temperature.

Experiment confirms Pauli's result, quantitatively as well as qualitatively. Pauli's theory leads to the following expression for the susceptibility :

$$\text{susceptibility} = 3 \left(\frac{\pi}{3} \right)^{\frac{3}{2}} \mu_0^2 n^{\frac{1}{2}} m_0 h^{-2}$$

where
$$\mu_0 = \frac{eh}{4\pi mc}.$$

Substituting the numerical values of the constants, we find for the susceptibility of Na, K and Cs the values 0.66, 0.52, 0.45 against the experimental values 0.65, 0.54, 0.42 (to convert to absolute units, these numbers must be multiplied by 10^{-6}). This result provides a further proof of the validity of Fermi's statistics for the conduction electrons in metals.

* Pauli, *Zeits. f. Physik*, 41, 81, 1927.

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CONCLUDING REMARKS

SCIENCE began by being a simple record of observations, and it has long retained this characteristic of its early years, continuing to be closely bound up with what is evident to our senses ; it has, however, tended to break away more and more completely from this limitation ; in proportion as it widens its field and probes matters more deeply, it becomes more abstract and attains a greater generality, to such an extent that it is only possible to follow it by dint of lengthy and laborious effort. It makes herculean efforts to interpret the infinitely complex universe of direct human experience in terms of simple fundamental laws ; its aim is to reduce the complicated to the simple, and when a fresh position has been won our mind contentedly surveys the order which supersedes the former apparent chaos, although the why and wherefore remain unanswered as before. The supreme architect who can unite all known phenomena in one harmonious structure, revealing their mutual relationships and causes, is yet to come ; in the development of scientific thought, what has been won in the past is not destroyed, but is elaborated so as to form the starting point for fresh lines of progress to which there is no limit as far as the eye can see.

Relativity, the theory of quanta, wave-mechanics, the new statistics . . . What remains of the old division of Physics into Mechanics—the region of muscular energy—, Heat—dominated by the sense of touch—, Sound—the science of hearing—, and Light—the science of vision ?

In mechanics itself the original idea of Force fades away before the more or less intangible notion of Energy ; in Optics our eyes are reduced to dealing with an insignificant portion of the vast range of radiations, and in Acoustics the same thing has happened with regard to the ear.

The first branch of physics to develop during the early period was mechanics, which dealt with the movement of bodies, and this was undoubtedly due to the greater amount of information which could be obtained on this subject; the other great divisions of physics, viz., acoustics, optics and the theory of heat, developed more slowly, while slower still in growth were the new branches of electricity and magnetism in which—as Langevin points out—practically nothing is directly accessible to our senses except by the intervention of some mechanical process.

The independence of the various branches of physics, although it is apparent rather than real, has resulted in the development of separate theories to co-ordinate and explain the facts belonging to each individual branch. The interpretation of the sensation of sound as the effect of vibrations, however, enabled acoustics to be linked immediately with mechanics, and this provided one of the first examples of the mutual interaction of two branches of physics; further, Newton's genius brought astronomy under the laws of mechanics at a single stroke. A new and important result of the same kind was obtained when the kinetic theory was developed, when heat was interpreted as consisting of the movements of molecules or atoms; thus mechanics triumphed over the caloric theory and—thirty years ago—no one doubted that the same thing would happen in the case of optics, electricity and magnetism.

The last great workers in physics at the end of the nineteenth century—Righi, Kelvin, Helmholtz, Boltzmann, Rayleigh, Van't Hoff, Michelson, Ostwald, Boussinesq and Lorentz—thought probably that, in view of the wonderful harmony which their science exhibited and of the soundness of its principles, there would never be discovered any phenomena which lay outside those laws which seemed to include everything and within which every physical phenomenon ought to find a place.

Thus at the close of the nineteenth century it appeared—as Millikan remarked—that progress was to be expected, not by the discovery of new phenomena, but rather as the result of more exact measurements of the phenomena already discovered.

Clean contrary to this has been the rapid, entirely unforeseen

and, it may well be called, dramatic transformation which physics has undergone in the present century.

In each and every department experimental work of an ever more refined description has revealed new facts which new theories endeavour to explain and predict by making use of the most delicate and complex processes of mathematics.

“An innate tendency running right through this intense activity leads us towards a widespread unification which should, it seems, include not only all the branches of physics, as it used to be understood, but should also take in the kindred sciences of mechanics, chemistry, crystallography, astronomy and cosmogony.” *

This attempt to unite facts and theories and bring them into harmony with one another has taken us right through from the infinitely great to the vanishingly small; it has caused us, on the one hand, to probe the depths of the Universe, the temperatures, composition and evolution of the stars and nebulae, and, on the other hand, it has revealed to us the structure of atoms, those bodies which, although lowest in the scale of magnitudes, are yet complex systems containing electrons revolving about nuclei; moreover, it has demonstrated the still more wonderful fact that these nuclei are, in their turn, composed of particles of two kinds of electricity and split up explosively, giving rise to atoms of other elements. This explosion may be brought about, and matter may be disintegrated, by artificial means, the result being always the production of hydrogen. The old vision of a simple primordial basic constituent of matter has thus been realised.

Physics has at last succeeded in numbering and in weighing atoms and molecules; the elementary structure of crystals has been demonstrated and the electrical forces which hold their lattice frameworks in place have been analysed; just lately, unsuspected relations between matter and energy have been discovered and the inner nature of light has been investigated by Compton and by his followers.

One of the fundamental characteristics of the history of Science in recent years has been, strangely enough, to show that every

* Langevin, Preface to “*Où en est la Physique*,” by Courtines.

explanation founded on the classical mechanics is quite untenable throughout the whole range of electricity, magnetism and optics, which latter has been proved by Maxwell and Hertz to be a branch of electromagnetism.

The process of unification, although checked by this discovery, has not been entirely destroyed, but it has had to proceed in the opposite direction ; relativity showed that it was not the simplest phenomena of mechanics (those that were studied and classified first of all) which were the most fundamental in character ; after Einstein's genius had elucidated matters the opposite was seen to be the case : electrical and magnetic phenomena are the simplest and these lead to a mechanics which is more precise and more complete than the old mechanics.

Another new and unexpected development of recent years is the discovery of discontinuity in every branch of atomic physics ; it is the mysterious law of quanta which reigns supreme, and the discontinuity of atomic phenomena lies at the root of optics, electricity, magnetism and heat ; Planck's constant, appearing as it does in the most diverse phenomena, has brought out new connections between different branches of physics. Through Heisenberg's principle it shows what is the region of error, of inaccuracy inevitable in human observation, when we are investigating atomic phenomena.

On the empirical side the special features of twentieth century development in physics have been three in number ; the discovery and the development of the fact that radiation is, in certain respects, corpuscular ; the discovery of the existence of energy levels in atoms and in molecules, leading to the hypothesis of an atomicity additional to that already recognised in the case of electrons and protons ; the discovery that matter has certain of the characteristics of a wave-motion, first demonstrated in the well-known experiments of Davisson and Germer. The new mechanics is, in fact, the result of the work done by the theoretical physicists in order to provide a harmonious formal description of these new experimental facts and of the great mass of empirical data on which the " classical physics " of the nineteenth century was founded.

As to theoretical physics, it may be stated, in general terms, that this has outstripped the experimental side of the science so that many phenomena have been predicted theoretically and then verified as facts (*e.g.*, the collisions of the second kind, and the diffraction of electrons). We saw in Chap. VIII what theoretical and experimental ingenuity led to the prediction of the existence of two forms of hydrogen and to their separation in actual fact.

All these painstaking researches, these brilliant theoretical developments which have built up such wonderful new structures on the ruins of the old ones, create an impression of happy youthful exuberance and give hope of fresh progress, and the more so as the means available for research have been immeasurably augmented and improved.

THE NATURAL ORDER OF THE ELEMENTS WITH THEIR ATOMIC WEIGHTS

<i>At. No.</i>	<i>Element.</i>	<i>At. Wt.</i>
1	Hydrogen.	1.0077
2	Helium .	4.00
3	Lithium .	6.939
4	Beryllium.	9.02
5	Boron .	10.82
6	Carbon .	12.000
7	Nitrogen .	14.008
8	Oxygen .	16.000
9	Fluorine .	19.00
10	Neon .	20.2
11	Sodium .	22.997
12	Magnesium .	24.32
13	Aluminium .	26.96
14	Silicon .	28.06
15	Phosphorus .	31.024
16	Sulphur .	32.065
17	Chlorine .	35.458
18	Argon .	39.91
19	Potassium .	39.095
20	Calcium .	40.07
21	Scandium.	45.10
22	Titanium .	47.9
23	Vanadium .	50.96
24	Chromium .	52.01
25	Manganese .	54.93
26	Iron .	55.84
27	Cobalt .	58.97
28	Nickel .	58.69
29	Copper .	63.57
30	Zinc .	65.38
31	Gallium .	69.72
32	Germanium .	72.38
33	Arsenic .	74.96
34	Selenium .	79.2

ELEMENTS WITH THEIR ATOMIC WEIGHTS 397

<i>At. No.</i>	<i>Element.</i>	<i>At. Wt.</i>
35	Bromine	79·916
36	Krypton	82·9
37	Rubidium	85·44
38	Strontium	87·62
39	Yttrium	89·0
40	Zirconium	91·
41	Columbium (Niobium)	93·1
42	Molybdenum	96·0
43	Masurium	(—)
44	Ruthenium	101·7
45	Rhodium	102·91
46	Palladium	106·7
47	Silver	107·880
48	Cadmium	112·41
49	Indium	114·8
50	Tin	118·70
51	Antimony	121·77
52	Tellurium	127·5
53	Iodine	126·932
54	Xenon	130·2
55	Cæsium	132·81
56	Barium	137·37
57	Lanthanum	138·91
58	Cerium	140·25
59	Praseodymium	140·92
60	Neodymium	144·27
61	—	—
62	Samarium	150·43
63	Europium	152·0
64	Gadolinium	157·26
65	Terbium	159·2
66	Dysprosium	162·52
67	Holmium	163·4
68	Erbium	167·7
69	Thulium	169·4
70	Ytterbium	173·6
71	Lutecium (Cassiopeium)	175·0
72	Hafnium (Celtium)	178·6
73	Tantalum	181·5
74	Tungsten	184·0
75	Rhenium	(? 188)
76	Osmium	190·8
77	Iridium	193·1

398 *ELEMENTS WITH THEIR ATOMIC WEIGHTS*

<i>At. No.</i>	<i>Element.</i>	<i>At. Wt.</i>
78	Platinum	195·23
79	Gold	197·2
80	Mercury	200·61
81	Thallium	204·4
82	Lead	207·20
83	Bismuth	209·00
84	Polonium	(210)
85	—	—
86	Radon (Niton) (Ra-emanation)	222·
87	—	—
88	Radium	225·95
89	Actinium	(? 226)
90	Thorium	232·15
91	Protoactinium (Brevium)	(? 230)
92	Uranium	238·17

FUNDAMENTAL PHYSICAL CONSTANTS *

Velocity of light, c , 2.9986×10^{10} cm. sec.⁻¹.

Gravitation constant, G , 6.66×10^{-8} cm.³ gm.⁻¹ sec.⁻².

Charge of the electron, e , 4.774×10^{-10} e.s.u.

„ „ „ 1.592×10^{-20} e.m.u.

Specific charge of the electron, e/m , 5.305×10^{17} e.s.u. gm.⁻¹.

Vol. of the gram-molecule at 0° C., 22.4115×10^3 cm.³ mole.⁻¹.

Planck's constant, h †, 6.554×10^{-27} erg. sec.

Avogadro's number, 6.061×10^{23} mole.⁻¹.

Absolute zero, — 273.1 deg. C.

Gas constant, R , 8.315×10^7 erg. deg.⁻¹ mole.⁻¹.

Energy of translation of a molecule at 0° C., 5.620×10^{-14} erg.

Mass of the hydrogen atom, 1.663×10^{-24} gm.

Mass of the proton, M_p ‡, 1.662×10^{-24} gm.

Mass of the α -particle, 6.597×10^{-24} gm.

Stefan's constant, σ , 5.709×10^{-5} erg. cm.⁻² sec.⁻¹ deg.⁻⁴.

Boltzmann's constant, 1.372×10^{-16} erg. deg.⁻¹.

Wave-length of red cadmium line, 6438.4696 Ång.

Relative atomic weight of hydrogen, 1.0077.

Relative atomic weight of oxygen, 16.000 (by definition).

Grating space in calcite, 3.028 Ång.

Gram calory at 15° C., 4.185 joule.

* A recent discussion of the most probable values of the general physical constants has been published by R. Birge in the *Physical Review Supplement* for July, 1929.

† The three constants, h , c and e , are connected by the relation :

$$\frac{hc}{e^2} = \frac{2^5 \pi^{11/3}}{15^{1/3}}$$

as has been shown by Lewis and Adams (*Phys. Rev.*, 3, p. 92, 1914).

‡ The constants h , c , e , the mass M_p of the proton and the mass m_e of the electron are connected by the relation :

$$\frac{hc}{e^2} = \frac{M_p}{m_e} \cdot \frac{1}{\pi - 1}$$

as has been shown by J. Perles (*Naturwissenschaften*, 16, p. 1094, 1928).

400 *FUNDAMENTAL PHYSICAL CONSTANTS*

Wien's displacement constant, 0.2885 cm. deg.

Constant of the fine structure, $2\pi e^2/hc = 7.28 \times 10^{-3}$.

The magneton, $(h/4\pi)(e/m) = 0.91 \times 10^{-20} \text{ erg. gauss.}^{-1}$.

Radius of the normal orbit in the hydrogen atom, $0.5305 \times 10^{-8} \text{ cm.}$

Rydberg constant for hydrogen, $109677.7 \text{ cm.}^{-1}$.

Rydberg constant for ionised helium, $109722.2 \text{ cm.}^{-1}$.

Rydberg constant for infinite mass, $109737.1 \text{ cm.}^{-1}$.

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